Effects of Fly Ash on Mercury Oxidation During Post Combustion Conditions

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by

Glenn A. Norton, Hongqun Yang, and Robert C. Brown*
Dennis L. Laudal and Grant E. Dunham**
John Erjavec***
Joseph M. Okoh****

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*Center for Sustainable Environmental Technologies
284 Metals Development Bldg., Iowa State University, Ames, IA 50011

**Energy and Environmental Research Center
P.O. Box 9018, University of North Dakota, Grand Forks, ND 58202

***Department of Chemical Engineering
P.O. Box 7101, University of North Dakota, Grand Forks, ND 58202

****Department of Natural Sciences
3101 Carver Hall, University of Maryland Eastern Shore
Princess Anne, MD 21853

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ABSTRACT

Tests were performed in simulated flue gas streams using fly ash from the electrostatic precipitators of two full-scale utility boilers. One fly ash was from a Powder River Basin (PRB) coal, while the other was from Blacksville coal. Elemental Hg was injected upstream from samples of fly ash loaded onto filters housed in an oven at 120 or 180°C. Concentrations of oxidized and elemental Hg downstream from the filters were determined using the Ontario Hydro method. The gas stream composition and whether or not ash was present in the gas stream were the two most important variables affecting Hg oxidation. The presence of HCl, NO, NO_2, and SO_2 were all important with respect to Hg oxidation, with NO_2 and HCl being the most important. The presence of NO suppressed Hg oxidation in these tests. Although the two fly ashes were chemically and mineralogically diverse, there were generally no large differences in catalytic potential (for oxidizing Hg) between them. Similarly, no ash fraction appeared to be highly catalytic relative to other ash fractions. This includes fractions enriched in unburned carbon and fractions enriched in iron oxides. Although some differences of lesser magnitude were observed in the amount of oxidized Hg formed, levels of oxidized Hg generally tracked well with the surface areas of the different ashes and ash fractions. Therefore, although the Blacksville fly ash tended to show slightly more catalytic activity than the PRB fly ash, this could be due to the relatively high surface area of that ash. Similarly, for Blacksville fly ash, using nonmagnetic ash resulted in more Hg oxidation than using magnetic ash, but this again tracked well with the relative surface areas of the two ash fractions. Test results suggest that the gas matrix may be more important in Hg oxidation chemistry than the fly ash composition.

Combustion tests were performed in which Blacksville and PRB fly ashes were injected into filtered (via a baghouse with Teflon bags) flue gas obtained while firing PRB coal in a 35 kW combustor. The Ontario Hydro method was used to determine the Hg speciation after fly ash injection. Wall effects in the combustor complicated interpretation of testing data, although a number of observations could still be made. The amount of Hg collected in the Ontario Hydro impingers was lower than anticipated, and is probably due to sorption of Hg by the fly ash. While firing PRB coal without any ash injection, the percent oxidized Hg in the gas stream was fairly high (average of 63%). The high levels of vapor phase oxidized Hg in these base line tests may be due to catalytic effects from the refractory materials in the combustor. When PRB fly ash was injected into a filtered PRB flue gas stream, the percentage of oxidized Hg in the gas stream decreased dramatically. Decreases in the percentage of oxidized Hg were also observed while injecting Blacksville fly ash, but to a lesser extent. Injecting whole Blacksville fly ash into the filtered PRB flue gas appeared to result in greater concentrations of oxidized Hg relative to the tests where whole PRB fly ash was injected. However, because the Blacksville fly ash has a relatively high surface area, this may be only a surface area effect.

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EXECUTIVE SUMMARY

The effects of fly ash on Hg chemistry in flue gas streams were investigated. Tests were performed in simulated flue gas streams using fly ash from the electrostatic precipitators of two full-scale utility boilers. One fly ash was derived from Wyodak-Anderson coal from the Powder River Basin (PRB), while the other was derived from Blacksville (Pittsburgh No. 8 seam) coal. Whole fly ash samples, sized fly ash, and magnetic and nonmagnetic concentrates from the fly ashes were analyzed for morphology, chemical composition, mineralogical composition, total organic carbon, porosity, and surface area. The Blacksville ash had a significantly higher surface area and a much higher unburned carbon content than the PRB ash. Only the Blacksville ash contained magnetic phases, and those phases were present almost entirely in the largest size fraction. For the Blacksville ash, the surface area of the nonmagnetic phases was substantially higher than that of the magnetic phases in the same size fraction. Mineralogically, the Blacksville ash was composed predominantly of magnetite, hematite, quartz, and mullite, while the PRB ash contained mostly quartz with lesser amounts of lime, periclase, and calcium aluminum oxide. The PRB fly ash contained no detectable Fe-bearing minerals.

Continuous streams of elemental Hg were injected upstream from samples of fly ash loaded onto filters housed in an oven at 120 or 180°C, and the effects of gas stream composition were investigated using simulated flue gas streams. Samples of whole fly ash, sized fly ash, and magnetic and nonmagnetic ash concentrates were used. Concentrations of oxidized and elemental Hg downstream from the filters were determined using the Ontario Hydro method. Retention of Hg on the loaded filters was negligible.

In the tests with simulated flue gas streams, **the gas stream composition and whether or not ash was present in the gas stream were the two most important variables affecting Hg oxidation**. The source of the ash also affected the results, but to a lesser extent. **Temperature was not a statistically important factor.** Based on statistical analyses of data obtained with a full-factorial design while using whole Blacksville fly ash at 180°C, **the most important gas affecting Hg speciation was NO_2, followed by NO and HCl**. However, the effect of NO depended on whether NO_2 was present or not. **The presence of NO appeared to suppress oxidation** and may play an important role in Hg chemistry. SO_2 was also important as a main factor, but was more important in its interaction with other gas components. Based on the statistical analyses, **all factors (i.e., gases) and two-way gas interactions were significant**. In addition, it appears that even the four-factor (the four gases noted above) interaction was statistically significant (although small).

In the bench-scale testing **with simulated flue gases, substantial amounts of Hg oxidation did not occur with either fly ash**, regardless of the temperature used for testing. In addition, **although the two fly ashes were chemically and mineralogically diverse, there were generally no large differences in catalytic activity (for oxidizing Hg) between them Similarly, no ash fraction appeared to be highly catalytic relative to other ash fractions** when using simulated flue gas. This includes fractions enriched in unburned carbon and fractions enriched in iron oxides. Although some differences of lesser magnitude were observed in the amount of oxidized Hg formed, **levels of oxidized Hg generally tracked well with the surface areas of the different ashes and ash fractions**. Therefore, although the Blacksville fly

ash tended to show somewhat more catalytic activity than the PRB fly ash, this could be due to the relatively high surface area of that ash. Similarly, for sized Blacksville fly ash, using the nonmagnetic ash from the largest size fraction resulted in more Hg oxidation than using the magnetic ash from the same size fraction. This may be due to the fact that the nonmagnetic phases had a higher surface area that the magnetic phases. However, the differences in the amount of oxidized Hg produced for magnetic and nonmagnetic concentrates from the first cyclone (largest sizes) catch were generally not substantial. Results from these tests suggest that **the gas matrix may be more important in Hg oxidation chemistry than the fly ash composition**.

Combustion tests were performed in which Blacksville and PRB fly ashes were injected into filtered (via a baghouse with Teflon bags) flue gas obtained while firing PRB coal in a 35 kW combustor. The Ontario Hydro method was used to determine the Hg speciation after fly ash injection. Wall effects in the combustor complicated interpretation of testing data, although a number of observations could still be made. The amount of Hg collected in the Ontario Hydro impingers was lower than anticipated for all of the tests. Similarly, the total Hg collected in the impingers was highest (but still lower than anticipated) in the tests performed without any ash injections. This is likely due to the sorption of Hg by the fly ash, and was particularly prominent when injecting PRB fly ash into the flue gas. **While firing PRB coal without any ash injection, the percent oxidized Hg in the gas stream was fairly high (average of 63%). The high levels of vapor phase oxidized Hg in these base line tests may be due to catalytic effects from the refractory materials in the combustor**.

Of the total gaseous Hg collected in the sampling impingers, the percentage of oxidized Hg varied considerably as the experimental conditions were changed. The lowest percentage of oxidized Hg (average of 19%) in the flue gas was observed when injecting PRB fly ash into the PRB flue gas stream. This suggests that **oxidized Hg was being preferentially captured by the fly ash being injected**. The decrease in the percentage of oxidized Hg in the gas stream was not as pronounced when injecting Blacksville fly ash, but was still apparent. Injecting whole Blacksville fly ash into the filtered PRB flue gas appeared to result in greater concentrations of oxidized Hg relative to the tests where whole PRB fly ash was injected. However, because the Blacksville fly ash has a relatively high surface area, this may be only a surface area effect, as appeared to be the case when using simulated flue gas streams. **Injecting magnetic and nonmagnetic Blacksville fly ash fractions into PRB flue gas gave comparable results** for the percentages of oxidized Hg in the flue gas stream (after the ash injection point). **However, definitive conclusions could not be drawn about relative catalytic effects between the two ash fractions in view of the data scatter and differences in the surface areas** between the two ash fractions.

INTRODUCTION

Mercury (Hg) is listed as a hazardous air pollutant (HAP) in the 1990 Amendments to the Clean Air Act. Coal-fired power generation emits on the order of 50 tons of Hg annually (1) and accounts for about a third of the total annual anthropogenic Hg emissions in the U.S. (2). In view of concerns over health and environmental impacts related to Hg, the U.S. Environmental Protection Agency has decided that Hg emissions from coal-fired power plants will be regulated. The relative concentrations of different Hg species present in coal combustion effluents are highly variable, and this is a major factor affecting Hg removal efficiencies by various conventional (e.g., wet scrubbers) and experimental (e.g., activated carbon injection) pollution control technologies. Unfortunately, the chemistry affecting the Hg speciation in effluents from coal utilization is poorly understood. Consequently, it is currently impossible to predict Hg removal efficiencies for any given Hg abatement technology (3). In order to better control Hg in these gas streams, a basic understanding of the chemistry of Hg under a range of thermal and chemical conditions is necessary.

It has recently become suspected that fly ash (e.g., fly ash from Blacksville coal) can play an important role in Hg chemistry by catalytically oxidizing some of the elemental Hg in the gas stream (4). However, the mechanisms by which fly ash affects the distribution of Hg species are unknown. The unburned carbon in fly ash is one important variable that has not been adequately addressed, and it could potentially be involved in the Hg oxidation mechanisms (5). A number of studies with activated carbon sorbents are also relevant to our work. For example, it appears that NO_2 may cause oxidation and desorption of Hg from activated carbon sorbents (6). In another study, activated carbon oxidized 95-100% of the elemental Hg in both simulated and actual flue gas streams from coal-fired combustors (7). Also, there appears to be substantial interactions between SO_2 and NO_2 with carbon-based sorbents, which results in rapid breakthrough of Hg and conversion of the Hg to an oxidized form (8). The unburned carbon in fly ash may result in similar oxidation mechanisms.

In other work, it was found that 40% of the elemental Hg (present at 40 ppb) in a stream of NO, O_2, and CO_2 was oxidized in the presence of either Al_2O_3 or SiO_2, while there was virtually no oxidation of the Hg when SO_2 was also present (9). When using a mixture of Al_2O_3, SiO_2, and Fe_2O_3, at least 80% of the Hg was oxidized, regardless of whether SO_2 was present. Thus, the inorganic components of fly ash require examination as well.

The HCl content of the flue gas is another important variable affecting Hg speciation, since coals high in chlorine generally appear to have more oxidized Hg in the flue gas than coals low in chlorine (10,11). Although the presence of HCl has been linked to the oxidation of Hg, the role of HCl and the specific reaction pathways are not completely understood (12). There are indications that the low-temperature oxidation of Hg is driven by the reaction of elemental Hg with Cl_2, where the Cl_2 is generated by catalytic reactions between HCl and char or other ash components (13). Equilibrium calculations on the relative percentages of elemental and oxidized Hg species have not been supported by field data, and the equilibrium seems to "freeze" prematurely (5). Because the oxidation of Hg in the presence of HCl is slow and proceeds only at high temperatures and high HCl concentrations, it is likely that the low temperature oxidation of Hg is catalyzed by metals in fly ash in the presence of HCl and/or NO_x (9).

The Hg chemistry in flue gas streams is very complex. The goal of this research was to provide fundamental information on post combustion flue gas chemistry to help predict Hg speciation in gas streams from coal-fired boilers. The focus of this work was to help identify major factors affecting Hg speciation, with an emphasis on the role of fly ash in the oxidation of elemental Hg. In addition to acquiring an improved understanding of the role of fly ash on Hg chemistry, a substantial amount of information was obtained on the role of various gases in the chemistry affecting Hg speciation in flue gas streams. For example, the effects of NO_x/HCl blends were included in this study because of the suspected synergistic effects between those gases (14). Bench-scale tests with simulated flue gas streams were used to study Hg speciation chemistry using rigidly controlled experimental parameters. In addition, tests with actual coal combustion flue gases were performed to acquire additional data related to Hg speciation. Results from these tests provided important information related to the chemistry associated with the oxidative conversion of Hg by fly ash. Through an improved understanding of the role of fly ash on Hg chemistry, it is hoped that this will in turn help predict Hg speciation in gas streams from coal-fired utility boilers. This will in turn lead to more accurate predictions on Hg removal efficiencies using both conventional and experimental Hg abatement technologies.

EXPERIMENTAL

Fly Ash Samples

Testing was performed with fly ash samples from the electrostatic precipitators (ESPs) of two full-scale utility boilers. One fly ash sample was obtained from a 65-MW front-fired pulverized coal boiler rated at 281,230 kg steam/hr (620,000 lbs steam/hr) at the Ames Municipal Power Plant (Ames, Iowa) while burning Wyodak-Anderson coal (subbituminous coal from the Rochelle Mine, Powder River Basin, Wyoming). That boiler has a hot-side ESP. The Powder River Basin (PRB) fly ash, which is tan in color, was collected while the boiler was at 90% of maximum load. The other fly ash was obtained from a 150-MW tangentially-fired pulverized coal boiler rated at 544,320 kg steam/hr (1,200,000 lbs steam/hr) at the AES Cayuga Plant (near Lansing, New York) while burning Pittsburgh No. 8 coal (bituminous coal from the Blacksville #2 Mine, Blacksville, WV). That unit uses a cold-side ESP. The Blacksville fly ash, which is a medium gray in color, was collected while the boiler was at 85-100% of capacity. For each fly ash, about 80 liters (20 gallons) of sample were collected. Although sample homogeneity was not expected to be a problem, each sample was homogenized by placing the ash in a 220-liter (55-gallon) drum, rolling the drum extensively, and periodically flipping the drum lengthwise. After mixing the ash in this manner, the ash was separated into several subsamples and stored in 20-liter (5-gallon) pails lines with plastic bags.

These fly ash samples were selected because of previous observations with similar ashes. For example, when Blacksville coal was burned at one site, over 80% of the Hg in the flue gas was observed to be in the oxidized form, which was believed to be partially due to the catalytic oxidation of Hg by the fly ash (15).   In that study, the effects of fly ash on Hg speciation was less pronounced when firing two western coals that were tested. Therefore, fly ash from a PRB coal was also selected for use in this study.

In some of the tests with the Blacksville fly ash, magnetic and nonmagnetic concentrates from the whole (unfractionated) fly ash were exposed to simulated flue gas streams. The PRB fly ash did not contain any highly magnetic fly ash components. Magnetic concentrates from the Blacksville ash were obtained by putting a layer of ash in a covered plastic petri dish. A hand magnet was placed directly on top of the lid and moved around randomly. This picked up only the magnetic ash. The side of the petri dish was tapped periodically to dislodge ash particles that were only weakly or moderately magnetic. This resulted in the retention of only the strongly magnetic ash fraction, which comprised 20% of the ash sample. Next, the cover of the petri dish was removed and the magnet was placed directly into the ash in the petri dish to remove essentially all particles with any significant degree of magnetism. The ash remaining in the petri dish after tapping or spinning the magnetic constituted the nonmagnetic fraction, which comprised 46% of the ash sample. For testing in simulated flue gas streams, the strongly magnetic ash and the nonmagnetic ash were used. This provided the most diversity in the mineralogical composition of the ash samples exposed to simulated flue gas streams.

Other tests were performed with sized Blacksville and PRB fly ash. Sizing was performed using a high-volume Source Assessment Sampling System containing a series of three cyclones to provide nominal cutoff diameters of 10, 3, and 1 microns for the first, second, and third cyclones, respectively. The first, second, and third cyclones collected 85-90%, 10-15%, and 1% of the total ash, respectively. Since the smallest cyclone contained only 1% or less of the total ash sample, only the ash samples from the first two cyclones were used for testing purposes. For the sized Blacksville fly ash, the ash in the first cyclone was also magnetically separated as discussed above. The catch in the second cyclone for the Blacksville fly ash contained no strongly magnetic phases. None of the size fractions for the PRB fly ash were magnetically separated because, as noted above, they did not contain any strongly magnetic phases.

Coal Samples

About 1360 kg (1.5 tons) each of Blacksville and PRB coals (see details above) were obtained for combustion tests. The raw coal had a top size of about two inches. Prior to combustion, each coal was ground using a jaw crusher, roll mill, and pulverizer containing a slotted screen. This produced a coal grind that was 40-45% minus 200 mesh (75 microns). Typical results from ultimate and proximate analyses on the PRB coal are given in Appendix 1. Although we had initially planned on performing tests while burning the Blacksville coal, problems were encountered during injection of that coal into the boiler. Therefore, no Hg testing was conducted while burning the Blacksville coal.

Bench-Scale Studies with Simulated Flue Gas

Flue Gas Simulator. A bench-scale testing apparatus was constructed to simulate flue gas streams from coal-fired power plants and to evaluate the potential for fly ash to oxidize elemental Hg in those streams. Photographs of the bench-scale system are shown in Figures 1 and 2, while a schematic diagram of the system is shown in Figure 3. A considerable amount of time was spent checking and confirming the proper operation of all components in the system and to ensure that sampling and analytical procedures were yielding high quality data.

Figure 1. Front End of Bench-Scale Testing System for Simulating Flue Gas Streams.

Figure 2. Back End of Bench-Scale Testing System for Simulating Flue Gas Streams.
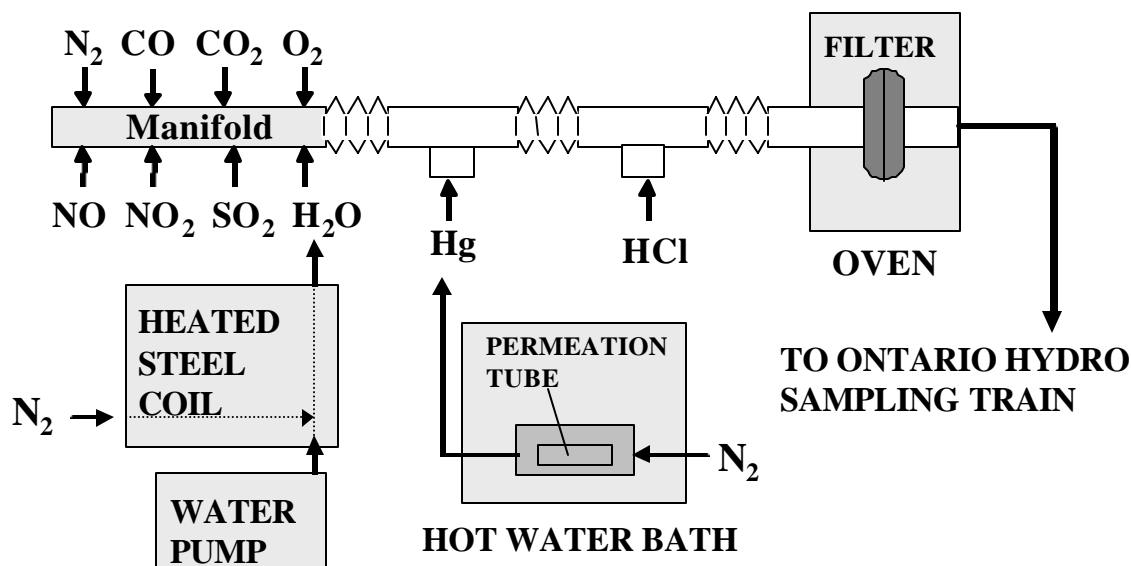
Figure 3. Schematic Diagram of Testing Apparatus used for Bench-Scale Studies.

The bench-scale apparatus for simulating flue gas streams consists of a stainless steel mixing manifold, a gas humidification system, a convection oven (Lindberg/Blue M Model G01310A) for heating the fly ash (loaded onto filters) to the desired temperatures, a series of impingers with absorbing solutions for collecting and speciating Hg, and finally a dry gas meter. The sample line carrying blended gases downstream from the manifold is constructed of corrugated PTFE Teflon. With the exception of HCl and Hg, gases were introduced into the mixing manifold and blended at that point. The HCl and Hg were introduced downstream from the manifold via Teflon union tees in the sample transport line. For HCl and Hg, all sample lines prior to the mixing tees were made of Teflon as well. The gas manifold and all sample transport lines downstream from the manifold were heated to 175°C (347°F). From the manifold, the gases were transported directly to the convection oven containing the filters loaded with fly ash. The filters were housed in Method 5 type filter holders with Teflon filter supports. Gases exiting the oven were immediately passed into impinger solutions to collect and speciate the Hg.

Nominal concentrations (in volume percent) of the gases used in the simulated flue gas matrix are shown in Table 1. Gases in the flue gas matrix were metered individually and included CO, CO_2, HCl, NO, NO_2, O_2, SO_2, and N_2 as the balance gas. Compressed gas cylinders were used for all of those gases. Other gases that could potentially be tested in the future include N_2O, SO_3, and Cl_2. Because of the hazardous nature of some of those gases, a ventilated enclosure on 24-hour emergency power was built and integrated into the system to house the gases of concern. Most of the gases were metered using 150-mm direct-reading rotameters. However, mass flow controllers (Aalborg AFC-2600 Mass Flow Controllers with an Aalborg 4PROC 4-Channel Command Module) were used for both the NO_2 and SO_2. Additional channels in the mass flow controller are available if desired.

Table 1. Concentrations of Individual Gases Used in the Simulated Flue Gas Streams.

GAS	CONCENTRATION IN FINAL GAS STREAM
CO	100 ppm$_v$
CO$_2$	12 %, molar
HCl	50 ppm$_v$
Hg	12 μg/m^3
H$_2$O	10 %, molar
NO	300 ppm$_v$
NO$_2$	20 ppm$_v$
O$_2$	6 %, molar
SO$_2$	1600 ppm$_v$
N$_2$	Balance

A certified elemental Hg permeation tube from VICI Metronics was used to generate the elemental Hg vapor. The certified Hg emission rate from the permeation tube was 175 $\pm$ 5 ng/min at 70.0°C (158°F). The permeation tube was housed in a VICI Metronics U-tube, which was heated in a covered water bath. The precision of the water bath is good to within 0.1°C (0.2°F), but was running slightly hotter that the temperature setpoint. This resulted in slightly elevated Hg emission rates. Therefore, the Hg emission rate at 70°C was experimentally determined by bubbling the gases into absorbing solutions over a precise period of time and then analyzing the solutions for Hg. The Hg emission rate was determined to be closer to 190 ng/min. A stream of nitrogen flowing at 200 mL/min continuously passed over the permeation tube and transported the evolved Hg to the main sample line, where it was introduced through a Teflon mixing tee.

A Milton Roy A961-361 SI Microprocessor Dosing Pump (solenoid diaphragm pump) added moisture to the gas stream by pumping water at a known and fixed rate into a stainless steel coil that was immersed in a hot oil bath in a metal can. The oil was heated to the desired temperature using a Glas-Col TM-636 700-watt Heating Mantle. By properly adjusting the temperature of the oil bath, the moisture was vaporized. A stream of nitrogen flowing at 2 L/min through the coil carried the moisture into the primary gas stream. Sufficient humidity was added to provide a moisture content in the final gas stream of about 10% on a volumetric basis. The percent moisture in the gas stream was calculated using equations 1 and 2 as shown below:

$$B_{wo} = V_w/(V_w + V_m) \qquad \text{Eq. 1}$$

$$V_w = 0.0474 \text{ ft}^3/\text{mL } (V_c) \qquad \text{Eq. 2}$$

where: B_{wo} = proportion by volume of water vapor in the gas stream, dimensionless
V_w = volume of water vapor collected at standard conditions, ft^3
V_m = dry gas volume through gas meter at standard conditions, ft^3
V_c = volume of water collected (assuming 1.0 g/mL of water), mL
Standard conditions = 530°R (70°F) and 29.92" of Hg

<u>Testing Approach</u>. Fly ash samples were loaded onto Whatman 9-cm (3.5-inch) QMA quartz microfiber filters using a Method 5 type filter holder connected to a section of 3.2-mm (1/8-inch) OD stainless steel tubing. The downstream side of the filter holder was connected to a GAST Model DOA-P104-AA vacuum pump. For each test, 0.6 g of ash were spread out into a thin layer on a clean, flat surface and the ash was suctioned up into the filter holder at a gas flow rate of 15 L/min. This gave an ash loading of 10 mg/cm^2. Other gas flow rates and sample loadings were tested, and this procedure was selected since it appeared to give the most even ash loading. Also, this procedure provided a good filter loading without reaching the point where the loading was too heavy and formed visible loose piles of ash on the filter. This allowed the filter to be mounted vertically in the convection oven without loss of any of the fly ash.

A continuous stream of elemental Hg was passed over the fly ash samples in the presence of different gas blends at a total dry gas flow rate of 15 L/min (roughly 32 ft^3/hr) for a period of 75 minutes. In addition to using the full gas blend (shown in Table 1), some tests were performed using only a "baseline blend" consisting of CO, CO_2, Hg, N_2, O_2, and H_2O. The baseline blend was considered to be nonreactive. Other tests involved adding specific reactive gases or combinations of reactive gases to the baseline blend. The reactive gases were HCl, NO, NO_2, and SO_2. When some of the gases in the simulated flue gas were eliminated to provide the desired matrix for specific tests, the flow of the N_2 balance gas was increased accordingly to maintain the 15 L/min nominal flow rate. All tests were performed in duplicate on the same day, and fresh portions of fly ash were used for each test. Many of the tests were also performed a third time, but on a different day. Prior to each test, the gases were allowed to equilibrate with the system. With the exception of Hg and HCl, the gases were allowed to equilibrate for a period of one hour. The HCl stream was allowed to equilibrate for two hours, while the Hg stream was allowed to equilibrate over night prior to use. Concentrations of elemental and oxidized Hg in the gas stream exiting the oven housing the loaded filter were determined using the Ontario Hydro Method, as described later in this report.

Tests were initially performed with the whole (unfractionated) PRB and Blacksville fly ash samples using both the "baseline blend" (everything but HCl, NO, NO_2, and SO_2) and the full gas blend. Those tests were performed at both 120 and 180°C (248 and 356°F). As a reference point and a quality control measure, tests were also performed using the full gas blend with blank filters. In addition, a limited number of tests were performed whereby magnetic and nonmagnetic concentrates from the unsized Blacksville fly ash were exposed to the full gas blend at 180°C.

Other tests were performed with the whole Blacksville fly ash at 180°C using a full factorial design whereby individual gases or combinations of gases were either present or absent in the gas blend. As gases were eliminated to provide the desired matrix for specific tests, the flow of the N_2 balance gas was increased accordingly to maintain the 15 L/min (dry) nominal flow rate. Based on the results of those tests, subsequent tests were performed using the baseline blend with NO_2, SO_2, and HCl (NO excluded) at 180°C using sized (first and second cyclone catches only) PRB and Blacksville fly ash, as well as magnetic and nonmagnetic concentrates from the sized fly ash. With regard to the magnetic and nonmagnetic concentrates, it must be emphasized once again that the PRB fly ash did not contain any highly magnetic material, so no

magnetic concentrates were available for that ash. Similarly, magnetic concentrates for the sized Blacksville ash were not available for the second cyclone catch. For the Blacksville fly ash, the different ash fractions were also exposed to various combinations of gases at 180°C. In particular, tests were performed using the baseline blend with various gases added. These gases were 1) NO_2 alone, 2) $NO_2 + HCl$, 3) $NO_2 + SO_2$, and 4) $NO_2 + SO_2 + HCl$.

Coal Combustion Tests

Coal Combustor. A 35 kW laboratory scale, down-flow combustor was used to study Hg oxidation chemistry in actual coal-derived flue gas streams. Shakedown tests with coal firing (using a PRB coal) indicated that coal could easily be burned in this combustor without any auxiliary fuels to sustain combustion. A schematic diagram for the laboratory scale combustor is shown in Figure 4, while a photograph of the combustor is shown in Figure 5. The combustor is about 3.6 meters (about 140 inches) high and contains a SiC firetube from Kromschroder. The refractory material is an alumina/silica ceramic purchased from A.P. Greene, and contains about 0.7% alkalis, 58.1% alumina, 1% iron oxide, 3.1% lime, 0.2% magnesia, 35.3% silica, and 1.6% titania. Because common refractory materials may cause catalytic oxidation of elemental Hg in our tests, the composition of the refractory material is worth noting. For example, the Al_2O_3 and TiO_2 in some boiler refractory materials are suspected catalysts (16). The combustor has the capability to entrain solids into the primary air flow and to inject chemicals into the secondary air flow. Several auxiliary injection ports are also available for the addition of solids or gases to meet experimental needs. A water-jacket heat exchanger is used to cool the gases exiting from the boiler. The heat exchanger is a 117-cm (46 inches) length of pipe consisting of an inner pipe that is 15.2 cm (6 inches) in diameter and an outer pipe that is 25.4 cm (10 inches) in diameter. Water is introduced co-currently into the water jacket. The combustor is equipped with a variety of on-line, real-time gas analyzers. These include nondispersive infrared analyzers (NDIR) for CO, CO_2, and SO_2; a chemiluminescence analyzer for NO, NO_2, and total NO_x; and an electrochemical O_2 analyzer.

In order to meet specific needs of this project, a number of modifications were made to the combustor, including adding feeders for coal and ash injections into the system. The combustor was equipped with two small pulse-jet baghouses (see Figure 6) containing Teflon filter membranes from W. L. Gore. Each baghouse has an air-to-cloth ratio of about 5.5 and is designed for a flow of up to 60 CFM. The bottom of each baghouse is fitted with a 3" full-port ball valve for ash removal. The first baghouses is for filtering fly ash from the coal being burned in the combustor. The second baghouse is located further downstream and is for removing fly ash injected into the clean flue gas stream (i.e., for removing fly ash injected into the clean gas stream at the exit of the first baghouse). The gas residence time inside either baghouse was calculated to be roughly 10 seconds. The temperature of the gas stream at the entrance to the first baghouse was about 230°C (445°F). Everything between the entrance of the first baghouse and the exit of the second baghouse was thermally insulated to minimize the temperature gradient across this zone. In addition, in order to reduce the temperature drop, the second baghouse was heat traced prior to insulating it. This provided a very consistent temperature of about 140°C (285°F) between (and including) the exit of the first baghouse and the exit of the second baghouse.

Assembled Furnace
(Gas Burner, Instrumentation,
External Insulation not shown)

Window (view hidden)

Thermocouple Port

Auxillary Gas Port

Feed Chamber

Removable Short Spacer

Removable Long Spacer

Thermocouple Ports

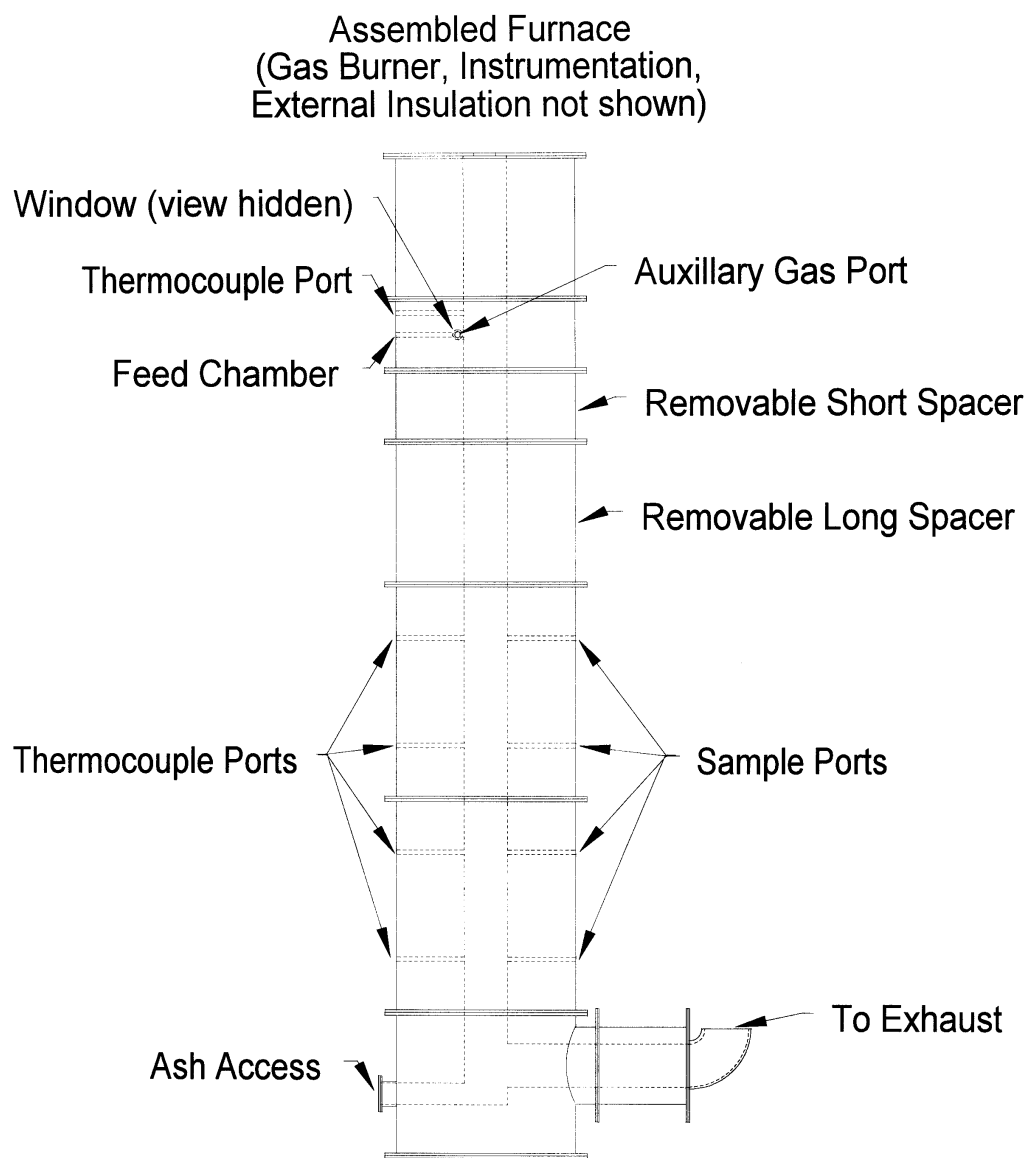Sample Ports

To Exhaust

Ash Access

Figure 4. Laboratory Scale Combustor used to Generate Actual Flue Gas Streams.

COMBUSTOR

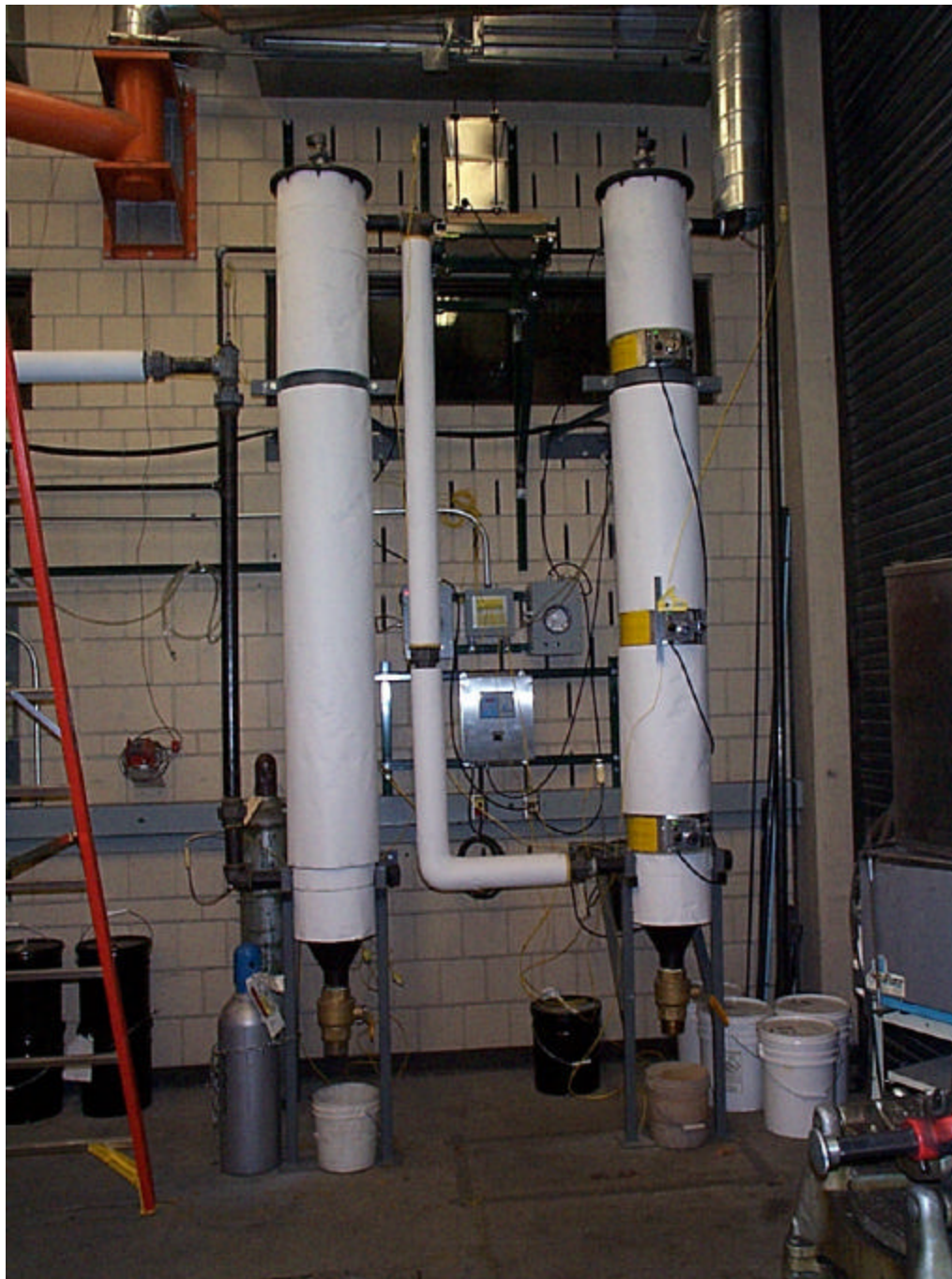Figure 5. Coal Combustor used to Generate Actual Flue Gas Streams.

Figure 6. Pulse-Jet Baghouses on the Coal Combustor.

<u>Testing Approach</u>. The general approach for the combustion tests was to burn the coal of choice and then use the first baghouse to filter the fly ash from the gas stream. This would provide an essentially particulate-free flue gas resulting from the combustion of that particular coal. Fly ash, either from the same coal or else from a different coal, was then injected into the clean flue gas matrix after the first baghouse but before the second baghouse. After injection of the fly ash into the filtered flue gas stream, the second baghouse removed the injected fly ash. The injected fly ash samples were from the ESPs of full-scale utility boilers and were the same samples used and discussed in the bench-scale work involving simulated flue gas streams. Sampling for Hg was then performed after the second baghouse to determine the distribution between elemental and oxidized Hg in the flue gas streams. No Hg sampling was performed prior to the first baghouse or in between the two baghouses. In addition, no mass balances for Hg were attempted in these tests.

The coal injection rate was selected based on a desired energy input rate into the boiler rather than on a coal weight basis. Powdered PRB coal was fed into the boiler at a rate of 5.4 kg/hour (about 12 pounds/hour) using a calibrated auger to transfer the coal into a pneumatic injection system. The pneumatic transport system consisted of a 1.3-cm (1/2-inch) diameter pipe with a stream of air for the carrier gas. An auger in an AccuRate 600 Series feeder was calibrated with PRB coal. The auger transferred powdered coal at a fixed rate into the air stream in the pipe, which then blew the coal into the boiler. The PRB coal could easily be burned without any combustion problems or coal feeding problems.

Working with the Blacksville coal proved to be more difficult. The properties of the Blacksville coal were much different than those of the PRB coal. Even when grinding the air-dried coal, the powdered coal was very sticky and more difficult to work with than the PRB coal. Although the Blacksville coal burned very well in the combustor, problems were encountered while pneumatically transporting the coal into the boiler, and the injection nozzle typically plugged up after feeding the coal for 15 minutes or less. Even after air drying the Blacksville coal to 2.3 % moisture, it was much stickier than the PRB coal. This moisture content is very low, and the coal transport problems are not due to the residual moisture content of the coal. Instead, it appears to be due to the inherent sticky nature of the coal itself, or to the volatile matter that is released as it nears the combustor. Also, because clogging of the transport system occurred right at the entry point into the boiler, the injection problems may have had something to do with swelling of the coal near the injection point into the boiler.

The injection problems with the Blacksville coal may have been compounded by the size of the pneumatic feeder (1.3-cm diameter steel tube) being used. Increasing the flow of injection air by almost 70% and decreasing the coal injection rate by about 10% (which achieved the lowest injection rate possible with the feeder being used) were tried in an attempt to inject the Blacksville coal into the boiler without clogging the injection tube. However, those attempts were not successful. Because of difficulties in burning the Blacksville coal, and because of time and monetary constraints, no tests were performed while burning that coal and no further attempts were made to solve the coal injection problem. Also, because Hg emissions from firing Blacksville coal are reportedly mostly in the oxidized form, thereby providing a less desirable

"baseline" when studying the effects of ash injection on Hg oxidation, elimination of the tests with the Blacksville coal did not significantly affect the study.

For the tests involving fly ash injection into the flue gas stream, the ash was injected immediately after the first baghouse. An auger was used to transfer the ash into the flue gas using an AccuRate 100 Series feeder. The auger was calibrated with whole (unfractionated) fly ash, and the auger rotation rate was set to provide an ash injection rate of about 8 grams/minute. This provided an ash loading of about 8 g/m^3 at process temperature and pressure. The residence time of the ash between the point of injection and the entrance to the second baghouse was about 0.8 seconds. The auger rotation rate was kept the same for all tests, even when injecting magnetic and nonmagnetic fractions of PRB fly ash. The fact that all of the ash injections were performed using the same auger rotation rate is an important consideration and will be discussed in the "Results and Discussion" section of this report.

Sampling Methodologies

Concentrations of total Hg, elemental Hg, and oxidized Hg downstream from the ash samples in the tests with simulated flue gas were determined using the Ontario Hydro method (17), which is known to require considerable experience and training in order to obtain reliable results (18). Similarly, Hg sampling was performed during all of the combustion tests using the Ontario Hydro method. The method involves using a series of eight impingers to collect and separate elemental Hg from oxidized Hg species. The first three impingers contain KCl absorbing solutions to preferentially collect oxidized Hg. The KCl impingers are followed by an impinger containing an aqueous mixture of HNO_3 and H_2O_2 to remove SO_2 and other unwanted gaseous compounds. That impinger is followed by a series of three impingers containing $H_2SO_4/KMnO_4$ absorbing solutions to collect elemental Hg. The final impinger contains silica gel desiccant to dry the gases before entering the dry gas meter. The sample line into the impinger train was heated to about 180°C to aid in the transport of oxidized Hg species. Sampling of simulated and actual coal combustion flue gas was performed for about 75 minutes for each test, and all tests were performed at least in duplicate.

Although the Ontario Hydro method provides good results with a high level of sensitivity, it requires a high level of quality assurance/quality control, requires well trained personnel, provides no real-time data, can have turnaround times of a week or more, and does not provide long-term results showing Hg emission variations. In view of these considerations, a continuous emission monitor (CEM) for Hg was obtained for use in this project. It was anticipated that the CEM would be used for all of the combustion tests and for a portion of the tests performed with simulated flue gas streams.

The CEM was a Tekran Model 2537A Mercury Vapor Analyzer, which can be used to provide data for both elemental and oxidized Hg concentrations when coupled to a suitable "front end" pretreatment system. The Tekran analyzer is based on first capturing Hg vapors onto gold-based collectors. The collected Hg is then thermally evolved into a cold vapor atomic fluorescence (CVAF) detection system. A high purity argon stream is typically used for this thermal evolution step. In order for that analyzer to work properly in flue gas environments (i.e., in the presence of NO_2 and acid gases such as HCl), the flue gas stream must be properly

conditioned prior to analysis. Although the gold traps collect both oxidized and elemental Hg, the NO_2 and HCl poison the collectors and give erroneous results for the Hg concentrations. To prevent this, it is necessary that the HCl (much easier to remove than NO_2) be removed before the sample gases pass through the gold trap. Also, if the instrument is to provide Hg speciation data, then the oxidized Hg must be removed from the gas stream so that the elemental Hg concentrations can be measured separately.

Gas stream conditioning was performed with a gas conditioning system made for ISU by the Energy and Environmental Research Center at the University of North Dakota (UND-EERC). The system, which was developed at UND-EERC, consists of an elemental Hg channel and a total Hg channel. In the elemental Hg channel, HCl and oxidized Hg are removed without removing any of the elemental Hg. In the total Hg channel, SO_2 and HCl are removed without affecting the Hg content of the gas stream, and all of the Hg is converted to the elemental form. Depending on which side of the pretreatment system the flue gas is passed through, either elemental Hg or total Hg in the raw sample gas is measured. After building the unit, personnel at UND-EERC provided the necessary training on the operation and maintenance of the conditioner.

After coupling the Tekran analyzer to the EERC gas conditioner, routine checks with the system were made while using simulated flue gas streams. Those tests were performed with clean (no fly ash) simulated flue gas streams to confirm the proper operation of the overall sampling/analytical system. Streams of elemental Hg vapor in nitrogen were passed through the entire gas conditioning system. As should always be the case under these conditions, the total Hg and the elemental Hg channels of the gas conditioner gave virtually identical results (i.e., no oxidized Hg is being formed, so the total Hg is the same as the elemental Hg). Next, simulated flue gas streams containing elemental Hg vapor were passed through the gas conditioner. In those tests, results from the elemental channel of the conditioner were much lower than the results from the total Hg channel of the conditioner (and the later was giving the correct values for total Hg concentrations). In fact, the readings from the elemental Hg channel of the conditioner slowly went to zero.

In the absence of fly ash, earlier work on this project showed that there is little or no Hg oxidation in the simulated flue gas. Therefore, numerous tests were performed to identify the reason for these anomalous readings from the elemental Hg channel of the gas conditioner. Various gases were added to the nitrogen individually, as well as in combination with other gases. Results obtained from both the elemental and total Hg channels of the gas conditioner were noted for each gas blend used. Results of those analyses are shown qualitatively in Table 2. As can be seen, there were no problems when using either channel of the analyzer when using blends of only NO_x and HCl, which is the gas blend where the traditional problems (poisoning of the gold cartridges used to collect Hg) are known to occur. Therefore, the gas conditioner clearly did an excellent job at taking care of this known problem. However, it was of interest to note that the Hg signals went to zero when analyzing gases from the elemental channel of the gas conditioner while using blends containing both SO_2 and NO_2. Normal Hg signals were obtained from the elemental Hg channel of the conditioner when using all other gas blends, and readings obtained while using the total Hg channel of the analyzer were always normal, regardless of the gas blend used.

Table 2.   Results of CEM Tests with Simulated Flue Gas Streams.

Gases Added to Nitrogen	CEM Response from Elemental Hg Channel of Conditioner	CEM Response from Total Hg Channel of Conditioner
HCl	OK	OK
NO	OK	OK
NO_2	OK	OK
SO_2	OK	OK
HCl + NO	OK	OK
HCl + NO_2	OK	OK
HCl + NO + NO_2	OK	OK
SO_2 + NO + NO_2	No Signal	OK
SO_2 + NO	OK	OK
SO_2 + NO_2	No Signal	OK
SO_2 + NO + NO_2 + HCl	No Signal	OK

After discussing the problem with research personnel at the EERC, we learned that they have also encountered this problem previously. However, they noted that the problem has been sporadic and unpredictable. The reason for the data anomalies that we observed is not known. Sometimes the problem crops up suddenly for reasons that are not understood, and sometimes the problem vanishes on its own. At other times, the problem persists and is difficult to correct. In one instance, replacement of the costly gold-based Hg collectors in the Hg analyzer appeared to eliminate the problem. These observations demonstrate the continuing need for additional research in the development of Hg CEMs for flue gas analyses. Funds were not available in this project for CEM development work. Therefore, in view of time and monetary constraints, combined with remaining uncertainties regarding the CEM and/or gas conditioning system, it was decided that the Ontario Hydro procedure would be used for Hg sampling throughout the entire project.

Sample Analyses

Scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDX) was used to examine the morphology and chemical composition of the fly ash samples. A Hitachi S-2460N SEM was coupled to an Oxford Instruments Isis Model 200 x-ray analyzer. The SEM was operated at an accelerating voltage of 20 kV and a beam current of 0.5 nA. This technique does not provide bulk ash composition since the sampling depth is on the order of 1 to 2 μm. Nonetheless, it does provide some valuable chemical information on the samples. Elemental scans were taken at low magnification to provide overall chemical concentrations for the samples. The chemical data are believed to be accurate to within about 20%. For a given element, the relative elemental concentrations observed between samples are believed to be reliable.

X-ray diffraction (XRD) was used to examine the mineralogical composition of the whole and fractionated fly ash samples. The scans were performed using a Siemens D500 x-ray diffractometer with Cu K-α radiation. For the XRD analyses, it is important to note that XRD identifies only crystalline components of the sample. This is important since coal combustion fly ash typically contains a considerable amount of glassy material.

BET measurements (using N_2 adsorption isotherms) were obtained on whole and fractionated fly ash samples with a Micromeritics Instrument Corporation Accelerated Surface Area Porosimeter 2010. The surface area (both external and micropore) and average pore diameter were determined.

Total organic carbon (TOC), or unburned carbon, was determined in the bulk fly ash samples using a Perkin Elmer TGA 7 Thermogravimetric Analyzer with a TAC 7/DX controller. About 25 mg of ash were heated to 750°C (1380°F) at a rate of 20°C/min (36°F/min) in nitrogen. The sample was held at that temperature until a constant weight was obtained, which took about 30 minutes. The gas stream was then switched to air while maintaining a temperature of 750°C. The weight loss observed in the presence of air was measured, which constituted the TOC content of the sample.

The impinger solutions from the Ontario Hydro sampling train were analyzed for Hg to determine the total amount of Hg collected and the percentages of elemental and oxidized Hg. The solutions were prepared for analysis using procedures specified in the Draft Ontario Hydro Method. Analyses for Hg in the impinger solutions were performed by conventional flow-injection cold vapor atomic absorption spectroscopy using a Leeman Labs PS200II Mercury Analysis System.

In addition to analyzing the impinger solutions, a variety of fly ash samples which had been exposed to simulated flue gas streams under a variety of test conditions were analyzed for Hg content. In order to know how much Hg was present in the fly ash prior to testing, portions of the PRB and Blacksville fly ashes which had not been exposed to simulated flue gas streams were also analyzed. Analyses for Hg levels in the fly ash samples were determined after leaching the samples with 20% HNO_3 (trace metal grade) for 60 minutes at 80°C (176°F). The procedure involved placing 1 gram of loose ash (for samples not exposed to simulated flue gas streams) or one half of a filter loaded with fly ash into a wide-mouth glass bottle. Next, 10 mL of the 20% HNO_3 was added to the bottles and the contents were swirled. The bottles were capped and placed in a preheated oven for one hour, swirling the contents about half way through. The bottles were then removed from the oven and allowed to cool to room temperature. At that point, roughly 35 mL of deionized water was added, followed by about 5 mL of 5% $KMnO_4$ solution. After standing for at least 15 minutes, hydroxylamine sulfate/sodium chloride solution was added until the solution cleared. The solutions were filtered through Gelman Sciences 25-mm, 1.0 µm Acrodisc Glass filters and then analyzed by conventional cold vapor atomic absorption using a Leeman Labs PS200II Mercury Analysis System. As a quality control measure, portions of NIST Standard Reference Material 1633b (fly ash) were always run with a set of samples. In addition, 500 ng Hg spikes were made into blank solutions and then run along with the other samples. Those spikes gave nominal Hg concentrations in the final solutions of about 10 ppb.

Statistical Analysis of Bench-Scale Data

     Statistical analyses were performed on all the Hg oxidation data (not just the test *averages* for a given set of experimental conditions) obtained while using the whole and fractionated fly ash samples in simulated flue gas streams. In other words, statistical analyses were performed using data from *all* of the replicate runs performed under a given set of experimental conditions. For the statistical analyses, the data were fit via least squares regression analysis to a full factorial model, with the factor levels being coded to lie in the range of -1 to +1. The data are shown in several ways. First, statistical "T values" are tabulated, as well as the probabilities of the results being due to chance occurrences. Second, Pareto charts are used as a graphical representation of the "T" values. Anything to the right of the dashed line (representing the "noise" level) in the Pareto charts is viewed as being statistically significant. The greater the effect, the farther the bars extend beyond the dashed line. Finally, line plots are yet another representation of the data. Both main effects plots and interaction plots are used. Main effects plots show what happens on average to the response when each one of the factors is changed from its low level (denoted by -1) to its high level (denoted by +1). The greater the slopes of the lines, the greater the effect. Because averages can be misleading, interaction plots are used to amplify main effects. Often the effect of one factor depends upon the value (level) of the others. The interaction plots show this phenomenon pairwise. For the interaction plots, the separation between the two lines in a given box shows the magnitude of the effects of one variable, while the slopes of the lines shows the effects of another variable (the larger the effect, the greater the slope). Interactions show up as differences in the slopes of the two lines in a given graph.

     Three series of analyses (Series 1, 2, and 3) were completed for the data obtained with the whole (unfractionated) fly ash samples in simulated flue gas streams. Table 3 shows the variables tested in each of the three statistical test series with the samples of *whole* fly ash. Tables 4, 5, and 6 show the experimental design for Series 1, 2, and 3, respectively. Similarly, Table 7 shows the variables tested for each of two test series (Series 4 and 5) involving the work with the *fractionated* fly ash samples, while Tables 8 and 9 give the experimental designs used for Series 4 and 5, respectively. All conclusions are based on statistical analyses performed at the 90% confidence level.

Table 3. Variables for Statistical Analysis of Data Obtained with Whole Fly Ash.

Test Series 1	Test Series 2	Test Series 3
Ash Type (PRB vs. Blacksville)	Ash Type (PRB vs. Blacksville)	SO_2 (0 vs. 1600 ppm)
Ash Included (Ash vs. No Ash)	Temperature (120° vs. 180°C)	NO (0 vs. 300 ppm)
Temperature (120° vs. 180°C)	Gas Composition (Baseline vs. Full Blend)	NO_2 (0 vs. 20 ppm)
		HCl (0 vs. 50 ppm)

Table 4. Experimental Design for Statistical Test Series 1.

Run No.	Ash Type	Temp. ($^\circ$C)	Hg^0 (%)
1	None	120	99
2	None	120	100
3	None	180	99
4	None	180	100
5	PRB	120	91
6	PRB	120	91
7	PRB	120	89
8	PRB	120	87
9	PRB	180	96
10	PRB	180	96
11	Blacksville	120	68
12	Blacksville	120	80
13	Blacksville	120	90
14	Blacksville	120	86
15	Blacksville	180	84
16	Blacksville	180	85

Table 5. Experimental Design for Statistical Test Series 2.

Run No.	Ash Type	Gas Composition	Temp. ($^\circ$C)	Hg^0 (%)
1	PRB	Baseline	120	100
2	PRB	Baseline	120	100
3	PRB	Baseline	180	100
4	PRB	Baseline	180	100
5	Blacksville	Baseline	120	100
6	Blacksville	Baseline	120	100
7	Blacksville	Baseline	180	100
8	Blacksville	Baseline	180	100
9	Blacksville	Baseline	180	100
10	PRB	Full Blend	120	91
11	PRB	Full Blend	120	91
12	PRB	Full Blend	120	89
13	PRB	Full Blend	120	87
14	PRB	Full Blend	180	96
15	PRB	Full Blend	180	96
16	Blacksville	Full Blend	120	80
17	Blacksville	Full Blend	120	86
18	Blacksville	Full Blend	180	84
19	Blacksville	Full Blend	180	85

Table 6. Experimental Design for Statistical Test Series 3.

Run No.	SO_2, ppm	NO, ppm	NO_2, ppm	HCl, ppm	Hg^0 (%)
1	0	0	0	0	100
2	0	0	0	0	100
3	0	0	0	0	100
4	1600	0	0	0	100
5	1600	0	0	0	100
6	1600	0	0	0	100
7	0	300	0	0	100
8	0	300	0	0	100
9	0	0	20	0	86
10	0	0	20	0	87
11	0	0	20	0	89
12	0	0	0	50	97
13	0	0	0	50	96
14	0	0	20	50	76
15	0	0	20	50	73
16	0	300	0	50	92
17	0	300	0	50	91
18	1600	0	0	50	98
19	1600	0	0	50	99
20	1600	0	20	0	76
21	1600	0	20	0	76
22	0	300	20	0	94
23	0	300	20	0	97
24	1600	300	0	0	100
25	1600	300	0	0	100
26	0	300	20	50	84
27	0	300	20	50	82
28	1600	0	20	50	70
29	1600	0	20	50	71
30	1600	300	0	50	95
31	1600	300	0	50	96
32	1600	300	20	0	95
33	1600	300	20	0	96
34	1600	300	20	50	84
35	1600	300	20	50	85

Table 7. Variables for Analysis of Data Obtained with Fractionated Fly Ash Samples.

Test Series 4	Test Series 5
Ash Type (PRB vs. Blacksville)	Cyclone 1 vs. Cyclone 2
Cyclone 1 vs. Cyclone 2	Magnetic vs. Nonmagnetic Ash
Magnetic vs. Nonmagnetic Ash	SO_2 (0 vs. 1600 ppm)
	HCl (0 vs. 50 ppm)

Table 8. Experimental Design for Statistical Test Series 4.

Run No.	Ash Type	Cyclone	Magnetic	Hg^0 (%)
1	Blacksville	1	Yes	77
2	Blacksville	1	Yes	80
3	Blacksville	1	No	73
4	Blacksville	1	No	72
5	Blacksville	2	No	71
6	Blacksville	2	No	70
7	PRB	1	No	87
8	PRB	1	No	87
9	PRB	2	No	80
10	PRB	2	No	81

Table 9. Experimental Design for Statistical Test Series 5.

Run No.	Magnetic	Cyclone	HCl	SO$_2$	Hg^0 (%)
1	Yes	1	None	None	94
2	Yes	1	None	None	94
3	Yes	1	Yes	None	92
4	Yes	1	Yes	None	92
5	Yes	1	None	Yes	80
6	Yes	1	None	Yes	80
7	Yes	1	Yes	Yes	77
8	Yes	1	Yes	Yes	80
9	No	1	None	None	90
10	No	1	None	None	89
11	No	1	Yes	None	75
12	No	1	Yes	None	76
13	No	1	None	Yes	78
14	No	1	None	Yes	79
15	No	1	Yes	Yes	72
16	No	1	Yes	Yes	73
17	No	2	None	None	87
18	No	2	None	None	85
19	No	2	Yes	None	82
20	No	2	Yes	None	80
21	No	2	None	Yes	64
22	No	2	None	Yes	64
23	No	2	Yes	Yes	71
24	No	2	Yes	Yes	70

RESULTS AND DISCUSSION

<u>Fly Ash Characterization</u>

In terms of particle morphology, the samples had the typical fly ash morphology and consisted predominantly of highly spherical particles. However, for the ash collected in the first cyclone, the Blacksville fly ash was substantially less homogeneous and contained more porous and irregularly shaped particles than the PRB fly ash. Differences between the two fly ashes were less pronounced for the catches from the second cyclone.

The SEM-EDX analyses of the Blacksville fly ash indicated that the Fe-rich (highly magnetic) phases in the first cyclone catch contained roughly 25% (weight) Fe, about 10% each of Al and Si, about 2% Ca, and lesser amounts of Na, S, K, and Ti. It is not surprising that the magnetic fraction has a significant amount of Al and Si. There is never a complete separation of iron oxides and aluminosilicate material due to particle cohesion during the separation process.

Also, significant amounts of Fe are typically dissolved (atomic substitutions) in a glassy aluminosilicate matrix. The nonmagnetic Blacksville fly ash fraction in the first cyclone catch contained only about 4% (weight) Fe, 10% Al, and 20% Si. As with the magnetic ash, the nonmagnetic ash fraction also contained about 2% Ca with lesser amounts of Na, S, K, and Ti. The chemical composition of the Blacksville fly ash from the second cyclone catch (all nonmagnetic) was very similar to the chemical composition of the nonmagnetic ash from the first cyclone catch.

For the PRB fly ash (all nonmagnetic), the ash from the first and second cyclones contained about 3% (weight) Fe, 10-20% Al and Si, about 10% Ca, and 2% or less of Mg, S, K, and Ti. The first cyclone catch was enriched in Si relative to Al, while the second cyclone catch contained roughly equimolar amounts of Si and Al.

The XRD results are tabulated in Appendix 2. The whole (unfractionated) Blacksville fly ash contained primarily quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), magnetite (Fe_3O_4), hematite (Fe_2O_3), a trace of lime (CaO), and possibly a trace of anhydrite ($CaSO_4$). The magnetic concentrate from the first cyclone catch of the sized ash contained the same minerals as noted for the whole ash, except for lime and anhydrite. As expected, there was an enrichment in the iron oxides relative to the quartz and mullite phases in that fraction. The nonmagnetic phases from the first cyclone contained the same minerals noted for the whole ash, but with an increased amount of lime. As expected, the nonmagnetic phases were enriched in quartz and mullite relative to the iron oxides. The mineralogical composition of the Blacksville fly ash from the second cyclone (all nonmagnetic) was very similar to that of the nonmagnetic ash from the first cyclone, although no lime was detected in the ash from the second cyclone. A substantial amount of amorphous (noncrystalline) material was evident in the ash collected in the second cyclone.

The PRB fly ash contained mostly quartz with lesser amounts of lime, periclase (MgO), calcium aluminum oxide ($Ca_3Al_2O_6$), and possibly a trace of anhydrite. No magnetite or hematite were detected. The sized fly ash in the first cyclone (all nonmagnetic) was very similar in composition to the whole ash in terms of mineralogy. The ash from the second cyclone (all nonmagnetic) was considerably different from that in the first cyclone in that it had substantially more amorphous material and relatively little quartz relative to the amounts of anhydrite, lime, periclase, and calcium aluminum oxide.

BET surface areas and average pore diameters for the whole and fractionated fly ashes are shown in Table 10. The surface area of the whole Blacksville fly ash was significantly higher than that of the PRB fly ash, and the surface area of the highly magnetic Blacksville fly ash in the first cyclone was substantially lower than the nonmagnetic phases in that cyclone fraction. Similarly, the fly ash from the second cyclone catch was substantially higher in surface area for the Blacksville fly ash as opposed to the PRB fly ash. For each whole fly ash sample, the BET measurements showed that about 70% of the total surface area was external surface area, with the remainder present as micropore surface area. The BET average pore diameter was comparable for the whole Blacksville and PRB fly ashes. The total surface area, external surface area, and micropore surface area generally tracked well with one another. In other words, a fraction that had a relatively high total surface area was also relatively high in the external and micropore surface areas.

Table 10. Results of BET Surface Area and Pore Diameter Measurements for the Blacksville and PRB Fly Ash Samples.

Sample	Surface Area (m^2/gram)			Ave. Pore Diameter (Å)
	Total	External	Micropore	
Blacksville Ash				
Whole	3.4	2.3	1.1	52
Cyclone 1				
Strong Magnetic	1.5	1.1	0.4	54
Nonmagnetic	4.8	3.3	1.5	45
Cyclone 2 (all nonmag.)	7.2	5.2	2.0	53
PRB Ash				
Whole	1.5	1.0	0.5	57
Cyclone 1 (all nonmag.)	1.7	1.0	0.7	43
Cyclone 2 (all nonmag.)	2.0	1.6	0.4	83

Table 11 shows results for the unburned carbon content of the fly ash samples. The whole Blacksville fly ash had about 3.6% unburned carbon, while the PRB fly ash contained less than 0.1%. Because the whole PRB ash had such a low unburned carbon content, no analyses for unburned carbon were performed on individual size fractions for that fly ash. As expected, the unburned carbon in the Blacksville fly ash was highly concentrated (by a factor of 10) in the nonmagnetic fraction of the first cyclone catch.

Table 11. Unburned Carbon in Blacksville and PRB Fly Ash Samples.

Sample	Unburned Carbon (%)
Blacksville Ash	
Whole	3.6
Cyclone 1	
Strong Magnetic	0.39
Nonmagnetic	3.9
Cyclone 2 (all nonmag.)	0.13
PRB Ash	
Whole	0.08
Cyclone 1 (all nonmag.)	not determined
Cyclone 2 (all nonmag.)	not determined

Data Uncertainties in Bench-Scale Tests

There are a variety of uncertainties that must be kept in mind when viewing the data obtained while using fly ash in simulated flue gas streams. The certification on the Hg permeation tube is only accurate to within $\pm$ 3% at the specified temperature. Also, although the water bath that is used to heat the U-tube containing the permeation tube has a precision of about 0.1°C, the temperature of the water bath appears to be accurate to only within 0.5°C. This, in itself, adds an uncertainty of roughly $\pm$ 5% in the Hg emission rate in view of potential day-to-day variations in the water temperature and other factors.

Other uncertainties in this work include 1) variations in gas concentrations due to metering errors, 2) analytical errors, which are on the order of 2-3%, 3) possible variations in the uniformity of fly ash loadings from test to test, and 4) sample preparation issues associated with the workup of the Ontario Hydro impinger solutions prior to analysis. Despite these issues, the percentages of oxidized and elemental Hg collected in the Ontario Hydro impingers were generally (95% of all cases) repeatable to within 2% (absolute) of the mean for a given set of experimental conditions. This is considered to be excellent in view of the numerous potential sources of error in this work and the known difficulties involved with the Ontario Hydro method. Because only major changes in Hg speciation are being sought in this work, the uncertainties mentioned above do not affect any of the conclusions drawn.

Another uncertainty that was considered is the possibility that significant amounts of Hg could be sorbed onto the ash during testing, and that the degree of sorption may not be consistent from test to test as the experimental variables were altered. Total Hg recoveries in the bench-scale tests generally (85% of all cases) ranged from 85 to 110%. Spot checks (using chemical leaching with subsequent analysis by cold vapor atomic absorption) on the Hg content of the fly ashes exposed to Hg in our tests indicated that there was little (less than 1% of the total Hg) or no Hg retention by the fly ash.

Results from Bench-Scale Testing

To simplify and clarify data presentation, only the mean values for the percentages of oxidized Hg observed under a given set of experimental conditions in the bench-scale testing are presented in this report. Since the percentages were determined on the Hg collected in the impinger solutions, the remaining Hg collected in the impingers is by definition all elemental Hg and need not be reported in the tables. Results obtained with both unsized and sized fly ash samples are discussed below.

Tests with Unsized Fly Ash. Results from the Ontario Hydro sampling for of the tests at temperature of 120° and 180°C using the baseline and full gas blends with unsized fly ash samples are shown in Table 12. Results of the tabulated statistical analyses for those data are shown in Tables 13 and 14. The data in Tables 13 and 14 are also shown as Pareto charts in Figures 7 and 8, respectively. For Test Series 2, the main effects line plots and interaction line plots are shown in Figures 9 and 10, respectively.

Table 12. Results Obtained Using the Baseline and Full Gas Blends with PRB and
          Blacksville Fly Ash*.

Conditions	Oxidized Hg (%)
Baseline Blend, PRB Ash, 120°C	0
Baseline Blend, PRB Ash, 180°C	0
Baseline Blend, Blacksville Ash, 120°C	0
Baseline Blend, Blacksville Ash, 180°C	0
Full Blend, Blank Filter, 120°C	<1
Full Blend, Blank Filter, 180°C	<1
Full Blend, PRB Ash, 120°C	10
Full Blend, PRB Ash, 180°C	4
Full Blend, Blacksville Ash, 120°C	19
Full Blend, Blacksville Ash, 180°C	16
Full Blend, Magnetic Blacksville Ash, 180°C	3
Full Blend, Nonmagnetic Blacksville Ash, 180°C	24

*All tests were performed with the whole (unfractionated) fly ash samples except
  for the last two data entries, in which magnetic and nonmagnetic concentrates
  from the whole ash were used.

Table 13. Statistical Analyses (Test Series 1) on Results Summarized in Table 12.

Variable	Effect	T-Value	Probability of Occurrence Due to Chance*
Ash Source	-10.00	-3.04	0.01
Ash Included	-23.50	-3.73	0.00
Temperature	0.00	0.00	1.00
Ash Source x Temp.	-1.50	-0.46	0.66
Ash Included x Temp.	5.00	-0.79	0.45

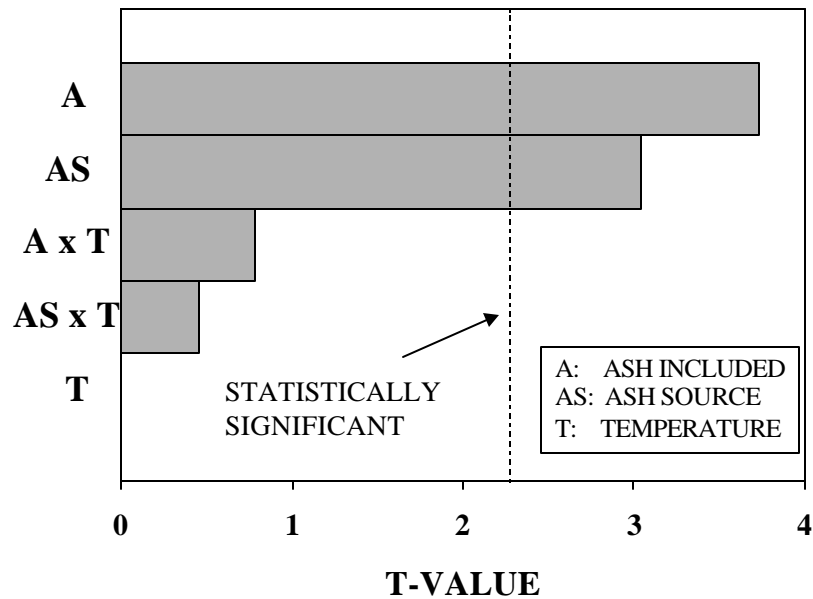* Expressed in percent as a decimal fraction, where 1.00 is 100%.

Figure 7. Pareto Chart for Statistical Test Series 1.

Table 14. Statistical Analyses (Test Series 2) on the Results Summarized in Table 12.

Variable	Effect	T-Value	Probability of Occurrence Due to Chance*
Ash Source	-4.50	-5.81	0.00
Gas Composition	-11.75	-15.16	0.00
Temperature	2.00	2.58	0.03
Ash Source x Gas Comp.	-4.50	-5.81	0.00
Ash Source x Temp.	-1.25	-1.61	0.14
Gas Comp. x Temp.	2.00	2.58	0.03
Ash Source x Gas Comp. x Temp.	-1.25	-1.61	0.14

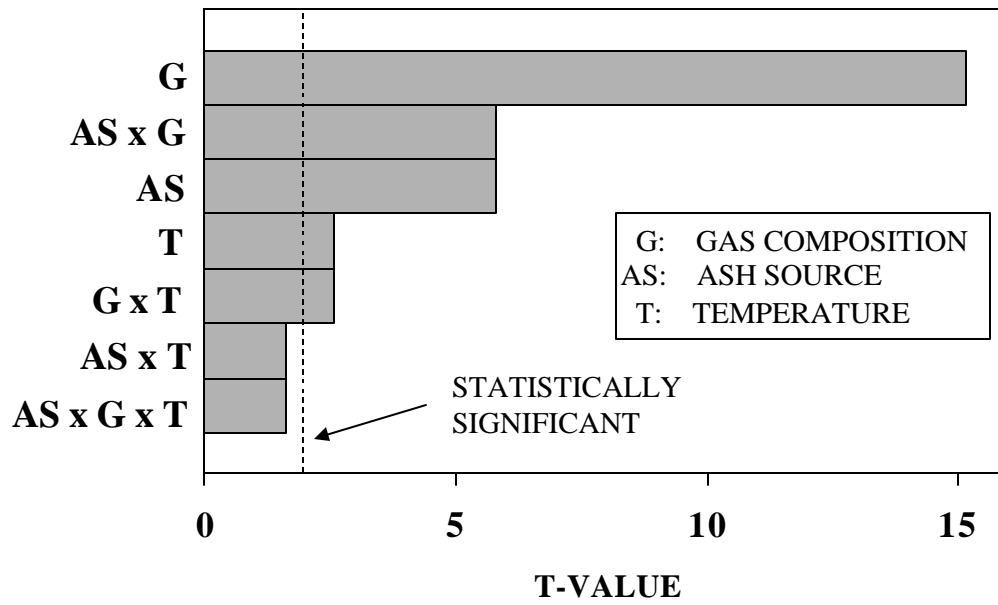* Expressed in percent as a decimal fraction, where 1.00 is 100%.

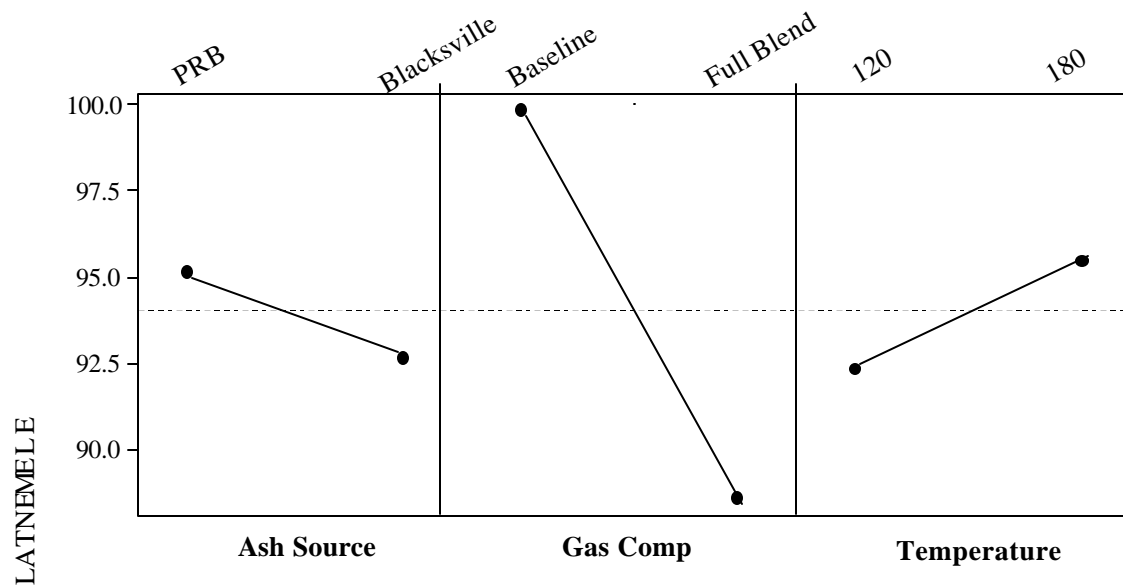Figure 8. Pareto Chart for Statistical Test Series 2.

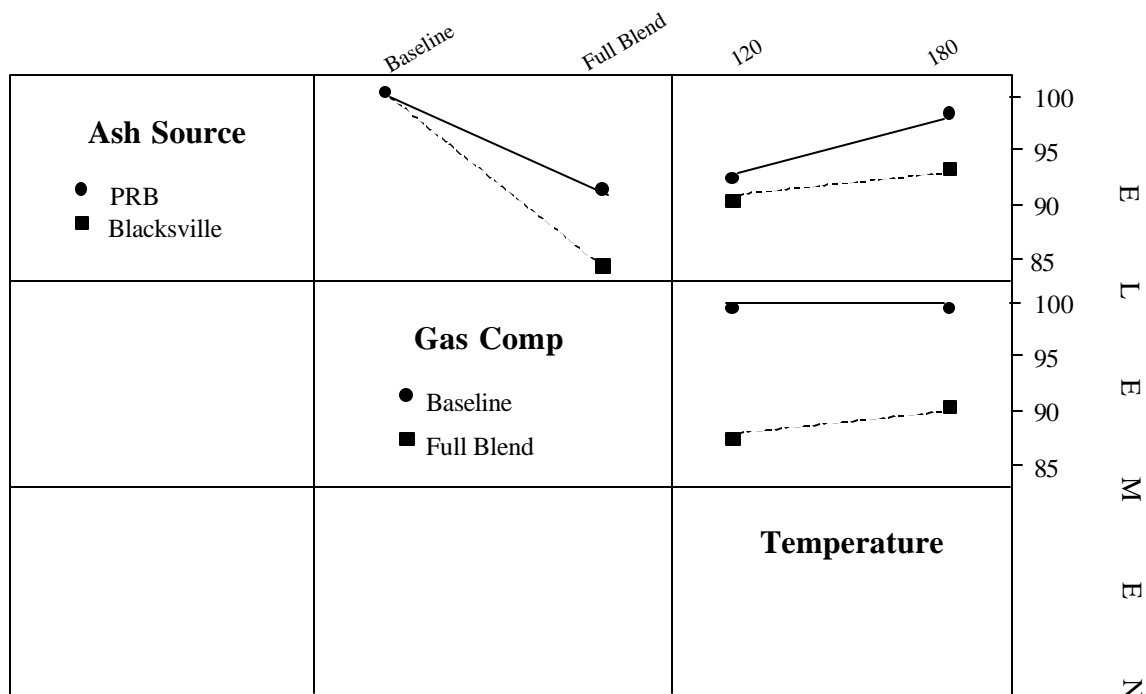Figure 9. Main Effects Plots for Statistical Test Series 2.

Figure 10. Interaction Plots for Statistical Test Series 2.

Based on the results in Table 12, it is evident that substantial amounts (i.e., >50%) of Hg oxidation were not observed. These observations agree with the growing body of data associated with Blacksville fly ash. Specifically, although the majority of the Hg in actual flue gases from the combustion of Blacksville coal appears to be in the oxidized form, the majority of the Hg in simulated combustion streams exposed to Blacksville fly ash is in the elemental form. No Hg oxidation was observed when using the baseline blend, regardless of which ash or which temperature (120 versus 180°C) was used. When using the full gas blend, there were hints of Hg oxidation even with blank (no ash) filters, but significant amounts of oxidation were observed only in the presence of fly ash. Thus, the most important factors were whether or not ash was present and whether the baseline blend or the full gas blend was used during testing.

Statistical analyses of the data summarized in Table 12 indicate that the source of the ash also affected the level of Hg oxidation, but to a lesser extent than the gas composition or presence of ash (see Figures 7 and 8). Also, there was a significant interaction between the source of the ash and the flue gas composition (see Figure 10). Temperature was not a statistically important factor for the two temperatures tested based on Test Series 1, and was only marginally significant based on statistical results from Test Series 2 (see Figures 7 and 8).

Passing the simulated flue gas over Blacksville ash resulted in more Hg oxidation than the PRB coal ash did. Although the whole Blacksville fly ash appeared to be slightly more catalytic than the PRB fly ash, this may simply reflect surface area differences (higher for Blacksville fly

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ash) between the samples rather than to something inherently unique with a particular fly ash sample. Because of the surface area issue that warrants closer examination, detailed chemical analyses on the ash samples are not warranted at this time. It is suspected that the surface area effects will outweigh the effects from factors such as surface trace element concentrations.

For the magnetic and nonmagnetic concentrates from the *unsized* Blacksville fly ash (see last two data entries in Table 12), using the nonmagnetic phases resulted in substantially higher amounts of oxidized Hg than the magnetic phases. Results indicated that the nonmagnetic phases resulted in 24% of the Hg being oxidized, while 3% of the Hg was oxidized when using the magnetic ash. It has been suspected that the magnetic (iron-rich) phases in fly ash would be more catalytic than the nonmagnetic (aluminosilicate-rich) phases because of its mineralogy (predominantly iron oxides) and possibly because the magnetic phases tend to be enriched in transition metals that could serve as oxidation catalysts. However, under the experimental conditions employed, our results do not support this.

Results obtained for magnetic and nonmagnetic fractions separated from *unsized* Blacksville fly ash correlate well with the relative surface areas between the two ash fractions. Although not presented in Table 10, the surface area for the *unsized* nonmagnetic ash was roughly four times that of the *unsized* magnetic ash. Therefore, the larger amounts of oxidized Hg obtained while using the nonmagnetic ash may reflect surface area differences between the magnetic and nonmagnetic fractions. Because of these surface area differences, caution must be exercised when drawing conclusions about the relative catalytic effects between the magnetic and nonmagnetic phases. Differences in the particle size distribution or pore size distribution may account for part of the differences in surface areas. However, differences in ash density between the magnetic and nonmagnetic phases must also be a contributing factor, since the filters were loaded with equal weights of ash. Because the magnetic phases are much more dense than the nonmagnetic phases, more particles of a given particle size of nonmagnetic ash would be loaded onto the filter than for the same particle size of magnetic ash, thereby resulting in greater surface area for the nonmagnetic ash loaded onto the filters.

As previously noted, the focus of this project was to identify fly ash components responsible for the catalytic oxidation of elemental Hg in flue gas streams. Consequently, when viewing the data, major differences in test results (i.e., percent of the total Hg that is oxidized) obtained under differing experimental conditions were being sought. Because major differences were not observed while using the full gas blend with either of the two fly ashes tested at 120° and 180°C, the next set of tests (involving a full factorial design), focused on using only the Blacksville fly ash at the higher of the two testing temperatures.

Results from the full factorial design testing with the Blacksville fly ash at 180°C are shown in Table 15, and results from the statistical analyses (Test Series 3) of those data are tabulated in Table 16. The results in Table 16 are also presented in the Pareto chart in Figure 11. However, for clarity of presentation, only the one and two component gas additions are included in that chart. Finally, main effects and interaction plots for the single gas additions are shown in Figures 12 and 13, respectively, in order to focus on the individual gas species and their relative impacts on Hg oxidation.

Table 15. Results of Full Factorial Design Tests (Test Series 3) with the Blacksville Fly Ash at 180°C.

Gases Added to Baseline Blend*	Oxidized Hg (%)
SO_2	0
NO	0
NO_2	13
HCl	4
HCl + NO_2	26
HCl + NO	8
HCl + SO_2	2
NO_2 + SO_2	24
NO_2 + NO	4
NO + SO_2	0
HCl + NO + NO_2	17
HCl + NO_2 + SO_2	30
HCl + NO + SO_2	4
SO_2 + NO + NO_2	4
SO_2 + NO + NO_2 + HCl	16

* Baseline Blend = N_2, O_2, CO, CO_2, and H_2O

Table 16. Statistical Analyses (Test Series 3) on the Results Summarized in Table 15.

Variable	Effect	T-Value	Probability of Occurrence Due to Chance*
SO_2	-0.98	-2.85	0.00
NO	5.27	15.33	0.00
NO_2	-14.40	-41.87	0.00
HCl	-7.48	-21.75	0.00
SO_2 + NO	2.35	6.85	0.00
SO_2 + NO_2	-2.48	-7.21	0.00
SO_2 + HCl	1.85	5.39	0.00
NO + NO_2	7.27	21.15	0.00
NO + HCl	-1.65	-4.79	0.00
NO_2 + HCl	-2.98	-8.66	0.00
SO_2 + NO + NO_2	1.85	5.39	0.00
SO_2 + NO + HCl	-0.48	-1.39	0.18
SO_2 + NO_2 + HCl	0.35	1.03	0.32
NO + NO_2 + HCl	0.35	1.03	0.32
SO_2 + NO + NO_2 + HCl	-0.98	-2.85	0.01

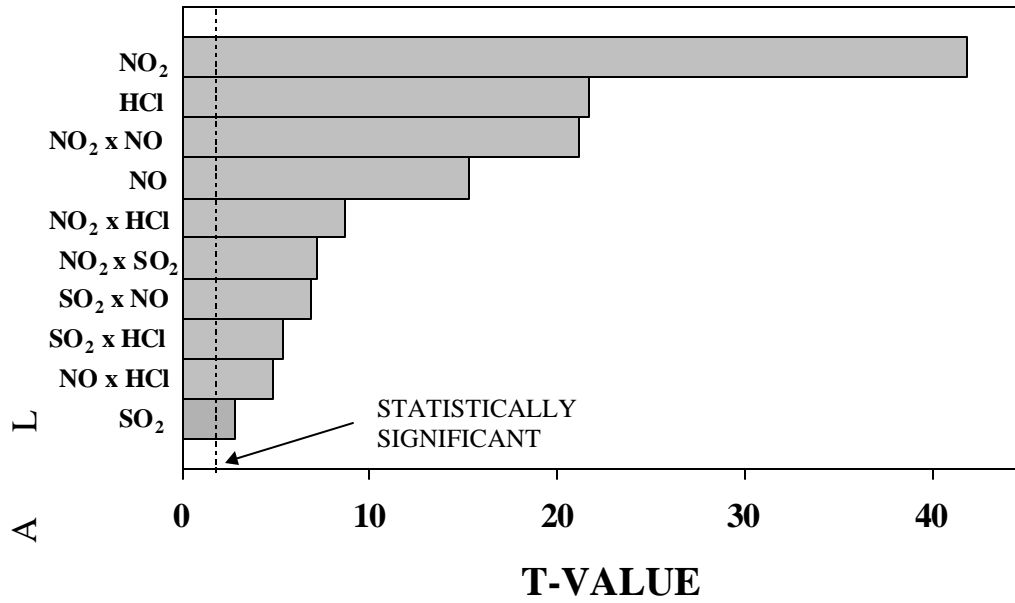* Expressed in percent as a decimal fraction, where 1.00 is 100%.

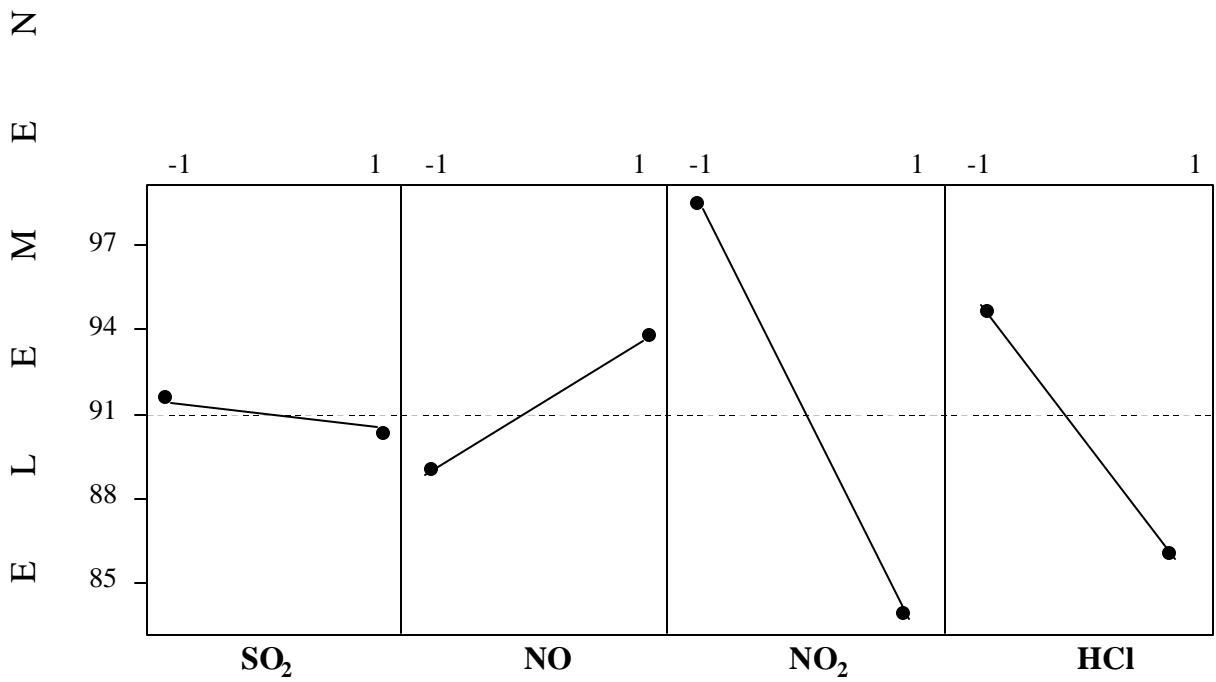Figure 11. Pareto Chart for Statistical Test Series 3.

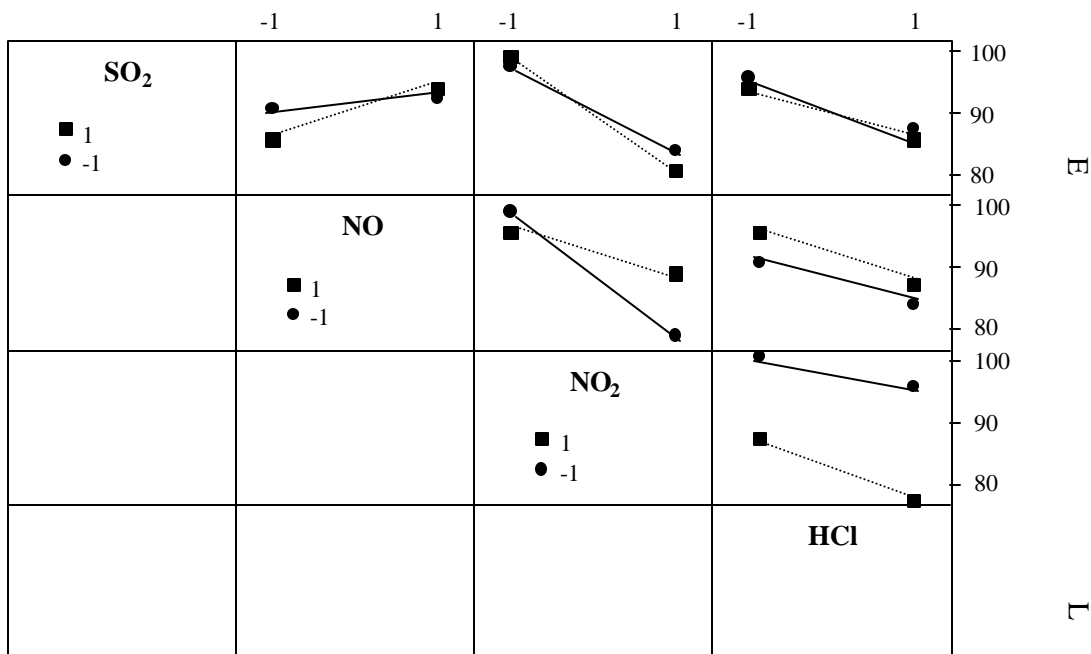Figure 12. Main Effects Plots for Statistical Test Series 3.

Figure 13. Interaction Plots for Statistical Test Series 3.

As shown in Table 15, the greatest degree of oxidation for the whole fly ash samples was observed when NO_2 was present with either HCl or SO_2 in the absence of NO. The synergistic effect of NO_2 and HCl can also be seen. This effect has been observed by other researchers as well. When NO_2 and HCl were added to the baseline blend, the amount of Hg oxidized was much higher than that obtained when summing the amount of Hg oxidized during the addition of HCl alone and NO_2 alone.

The statistical analyses of Test Series 3 (shown in Table 16) explore the gas stream composition in detail for the tests with Blacksville fly ash. Results of the analyses show that all factors and interactions (including the four-factor interaction) were statistically significant. Thus, this system is very complex. Of the gases added to the baseline blend, the gas species having the greatest effect on Hg oxidation was NO_2. Next in significance with respect to Hg oxidation were NO and HCl.

Although the presence of NO in the simulated flue gas stream was an important factor for Hg oxidation, the effect of NO depended on whether NO_2 was present. The bottom graph in the third column of Figure 13 shows that there was a large interaction between NO and NO_2, as shown by the large difference in slopes between the two lines. The bottom graph in the last column shows the large effect of NO_2 on Hg oxidation when HCl was present, as shown by the large separation between the two lines. However, the slopes of the two lines in that graph are not substantially different, so there was not a major interaction between the two gases.

Although the presence of SO_2 was statistically significant as a main factor, it was more important in its interaction with other gas components. These results are in agreement with work done by the EERC. In view of the complexity of the gas interactions with fly ash, the difficulties in understanding the Hg chemistry in coal-derived flue gas is not surprising. This is particularly true in view of the fact that the simulated flue gas system is still very simple compared to actual flue gas streams.

Another interesting observation is that, everything else being equal, the presence of NO actually appears to inhibit oxidation in the presence of other gases. For example, when only NO_2 and SO_2 were added, the amount of Hg oxidized was about 24%. However, when NO was also added without changing the NO_2 and SO_2 concentrations (the N_2 balance gas was decreased to compensate for the addition of each gas), the amount of Hg oxidized decreased to 4%. Similar effects can be seen for the tests with $NO_2 + SO_2 + HCl$ with and without the addition of NO. For emphasis, the amount of Hg oxidation observed in the absence and in the presence of NO for various gases (added to the baseline blend) is shown in Table 17. Thus, there is some evidence that the NO concentration may play a very important role in Hg oxidation chemistry in flue gases from coal combustion systems.

Table 17. Effects of Nitric Oxide on Hg Oxidation.

	Percent Oxidized Mercury	
Gases Added to Baseline Blend	**Without NO**	**With NO**
$NO_2 + SO_2$	24	4
$NO_2 + SO_2 + HCl$	30	16
$NO_2 + HCl$	26	17
NO_2	13	4

Tests with Sized Fly Ash. Results of tests with the sized fly ash fractions and magnetic and nonmagnetic concentrates from those ash fractions are shown in Table 18. As noted earlier, these tests were performed at 180°C with NO_2, SO_2, and HCl added to the baseline blend (there was not any NO added to the gas stream in these particular tests). That gas blend (baseline blend with NO_2, SO_2, and HCl added) was selected since it resulted in the greatest degree of Hg oxidation in the tests involving the full factorial design (see Table 15). By increasing the amount of oxidized Hg in the gas stream (after the fly ash) in this manner, it was hoped that differences in the catalytic potential between different fly ash fractions might be more readily observed.

Results of the statistical analyses (Test Series 4) on data obtained in those tests are shown in Table 19, while the Pareto chart for those statistical analyses is shown in Figure 14. The main effects and interaction plots are shown in Figures 15 and 16, respectively.

Table 18. Results of Tests using Sized Fly Ash and Magnetic and Nonmagnetic Concentrates
from those Size Fractions (Tests used the Baseline Blend Plus NO_2, SO_2, and HCl)

Sample	Oxidized Hg (%)
Blacksville Ash	
Cyclone 1, Magnetic	22
Cyclone 1, Nonmagnetic	28
Cyclone 2 (all nonmag.)	30
PRB Ash	
Cyclone 1 (all nonmag.)	13
Cyclone 2 (all nonmag.)	20

Table 19. Statistical Analyses (Test Series 4) on Results Summarized in Table 18.

Variable	Effect	T-Value	Probability of Occurrence Due to Chance*
Ash Source	12.25	15.81	0.00
Cyclone 1 or 2	-4.25	-5.49	0.00
Magnetic	6.00	5.48	0.00
Ash Source x Cyclone	-2.25	-2.90	0.03

*Expressed in percent as a decimal fraction, where 1.00 is 100%.
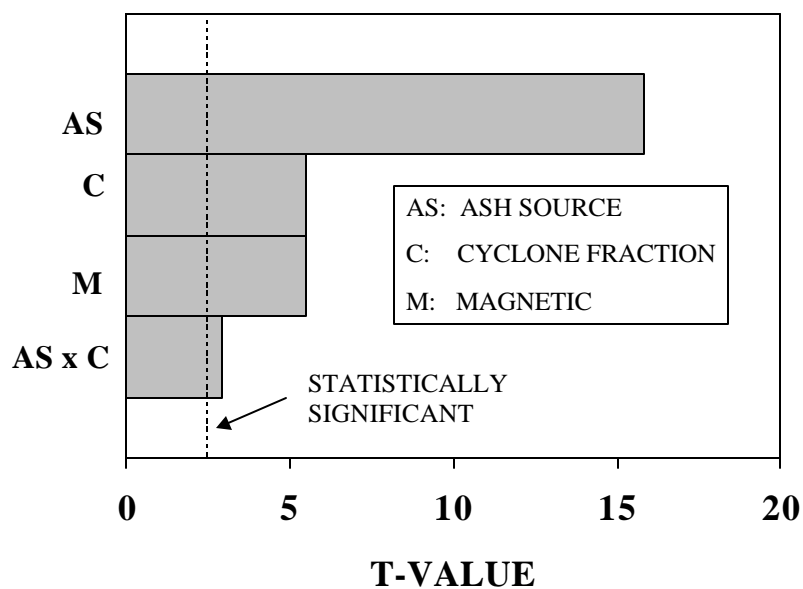

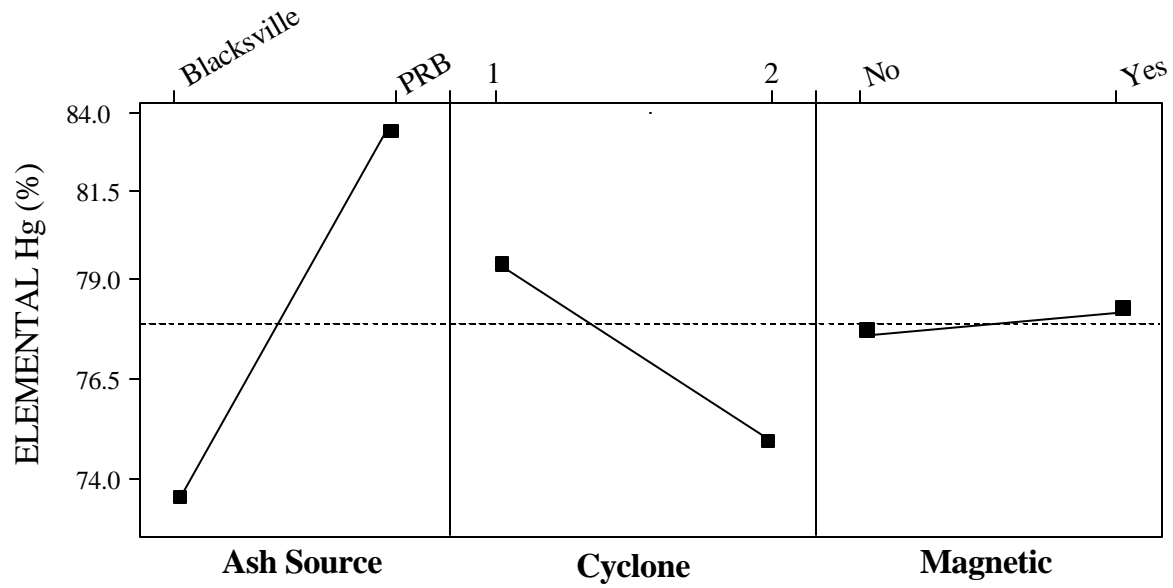Figure 14. Pareto Chart for Statistical Test Series 4.

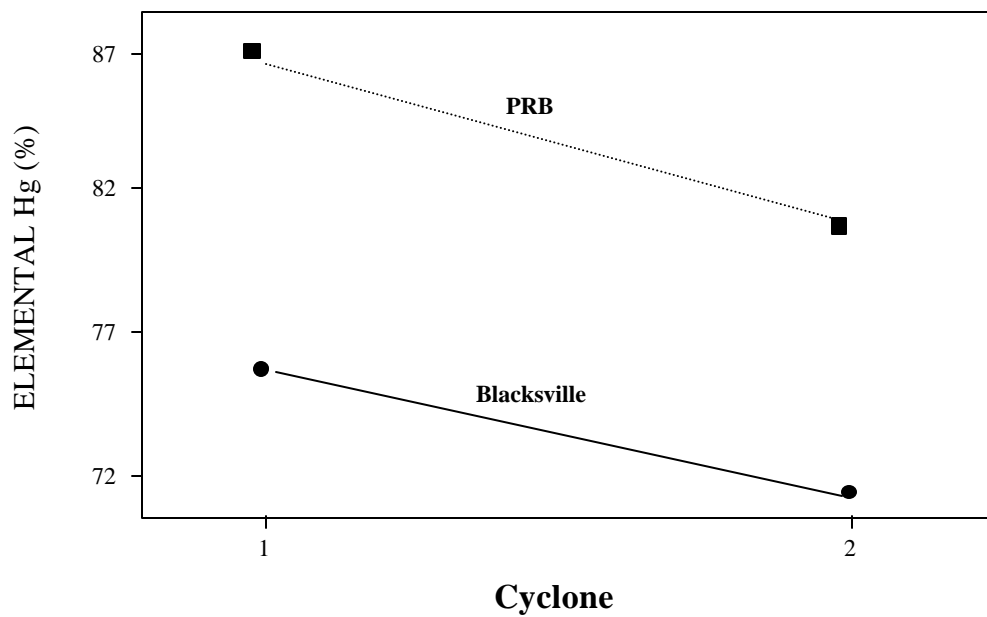Figure 15. Main Effects Plots for Statistical Test Series 4.

Figure 16. Interaction Plots for Statistical Test Series 4.

All factors were found to be statistically significant. The primary impact was from the ash source. There was a small but marginally statistically significant interaction between the ash source and the ash size fraction (cyclone 1 or 2).

With the gas blend used for these particular tests, the degree of oxidation observed between the magnetic and nonmagnetic concentrates from the Blacksville fly ash collected in the first cyclone were very similar (see results in Table 18), even though the later ash fraction had ten times the unburned carbon content as the magnetic fraction (see Table11). Therefore, the organic (unburned) carbon content does not initially appear to play a vital role in Hg oxidation chemistry based on these limited results. However, it is still possible that the organic carbon plays a role in the Hg oxidation chemistry to some extent. The unburned carbon in different ash fractions could potentially be chemically and/or physically much different from one another. The role of unburned carbon requires further investigation before any definitive conclusions can be drawn regarding its role in Hg chemistry.

As noted above, the nonmagnetic fraction (which was only present in the Blacksville fly ash) was only slightly more catalytic than using the magnetic fraction in these tests. Thus, these results are significantly different from those obtained using the full gas blend with magnetic and nonmagnetic concentrates from the *unsized* fly ash (see Table 12), where the nonmagnetic phases appeared to be much more catalytic than the magnetic phases. This could easily be related to differences in the experimental designs associated with each of the two sets of data. This includes differences in gas matrices used and differences in particle sizes used. As noted above, the data for the magnetic and nonmagnetic concentrates shown in Table 12 were obtained for concentrates from *unsized* ash. Therefore, all of the particle sizes for the nonmagnetic ash are being compared to the magnetic ash, which is present only in the largest particle sizes (first cyclone catch). Contrary to this, the data presented in Table 18 compare the magnetic ash (present only in the first cyclone catch) to only the *largest* size fraction of nonmagnetic ash. In this regard, it must also be noted that the tests with sized fly ash excluded the third cyclone catch because it represented only 1% or less of the total particulate catch. However, even though the amount of ash was very minimal, the surface area associated with that ash fraction (which was included in the nonmagnetic concentrates in Table 12) could be substantial.

The differences in the percent oxidized Hg observed for the various ash fractions shown in Table 18 tracked well (in a relative sense) with the respective surface areas of each ash fraction. However, the magnitude of the differences in surface areas between ash fractions did not always produce changes of equal magnitude in the percent oxidized Hg formed. This could be related to the analytical errors in either the surface area determinations or the Hg results. Alternatively, there may be significant differences in catalytic effects among the different ash fractions due to differences in chemistry and mineralogy, but those effects may be clouded by the surface area issues that appear to play a role in the Hg results.

Results obtained with different Blacksville fly ash fractions (sized ash, as well as magnetic and nonmagnetic concentrates from the sized ash) exposed to various gas blends at 180°C are shown in Figures 17 and 18. Results of the statistical analyses of those data are tabulated in Table 20, and are shown in graphical form as a Pareto chart in Figure 19. Finally, the main effects and interaction plots are shown in Figures 20 and 21, respectively.
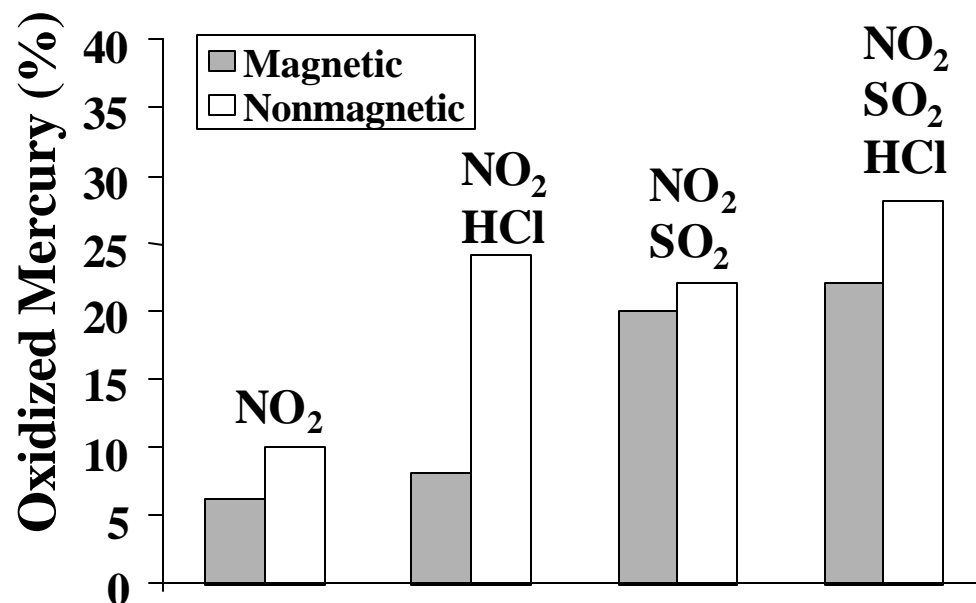
Figure 17. Comparison Between the Magnetic and Nonmagnetic Concentrates from the First Cyclone Catch using Blacksville Fly Ash.
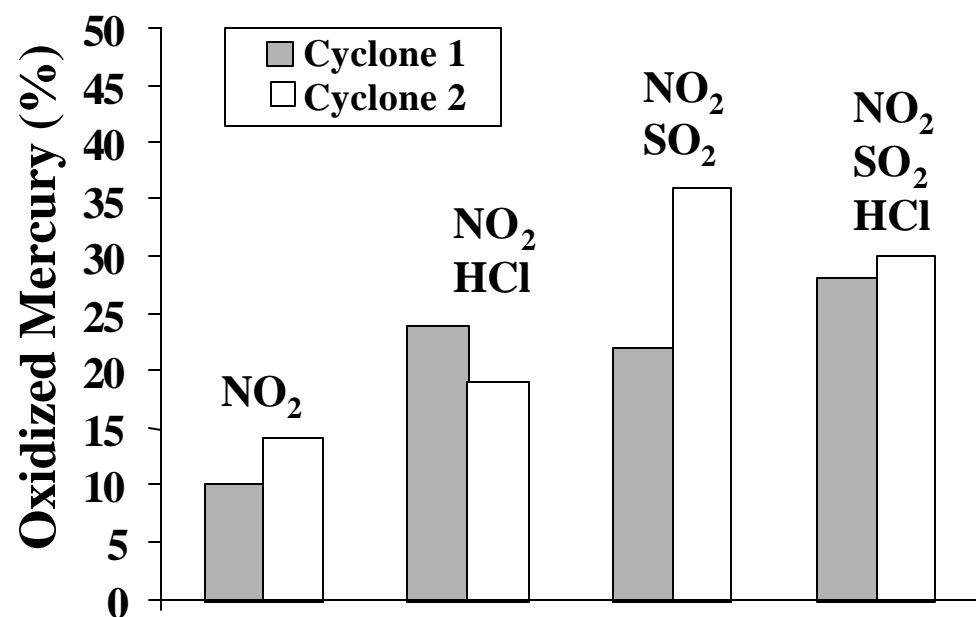
Figure 18. Comparison Between the Nonmagnetic Blacksville Fly Ash Fractions Collected in the First and Second Cyclones.

Table 20. Statistical Analyses (Test Series 5) on the Data Shown in Figures 17 and 18.

Variable	Effect	T-Value	Probability of Occurrence Due to Chance*
Magnetic	7.12	8.17	0.00
Cyclone Fraction	-3.62	-4.16	0.00
HCl	-0.50	-0.57	0.58
SO$_2$	-15.00	-17.20	0.00
Magnetic x HCl	4.12	4.73	0.00
Magnetic x SO$_2$	-3.38	-3.87	0.00
Cyclone x HCl	5.38	6.16	0.00
Cyclone x SO$_2$	-4.62	-5.30	0.00
HCl x SO$_2$	3.33	4.68	0.00

* Expressed in percent as a decimal fraction, where 1.00 is 100%.

Figure 19. Pareto Chart for Statistical Test Series 5.

Figure 20. Main Effects Plots for Statistical Test Series 5.
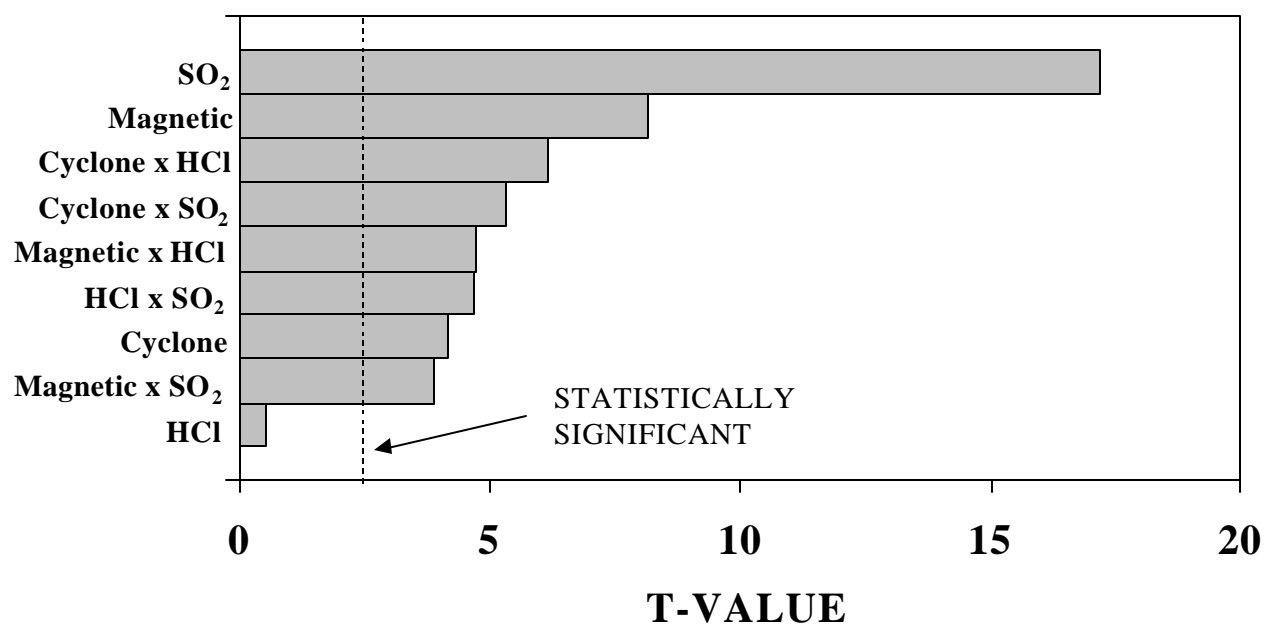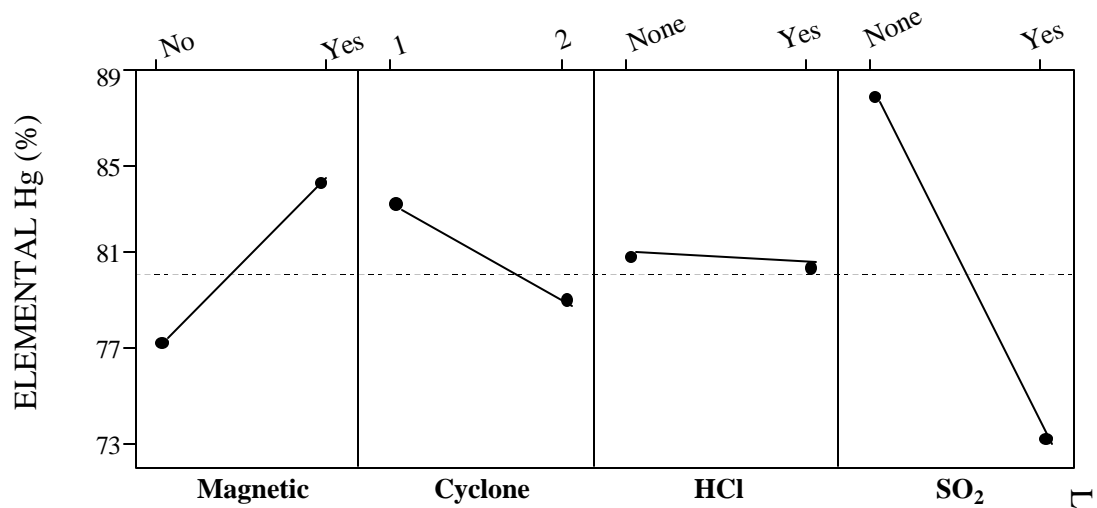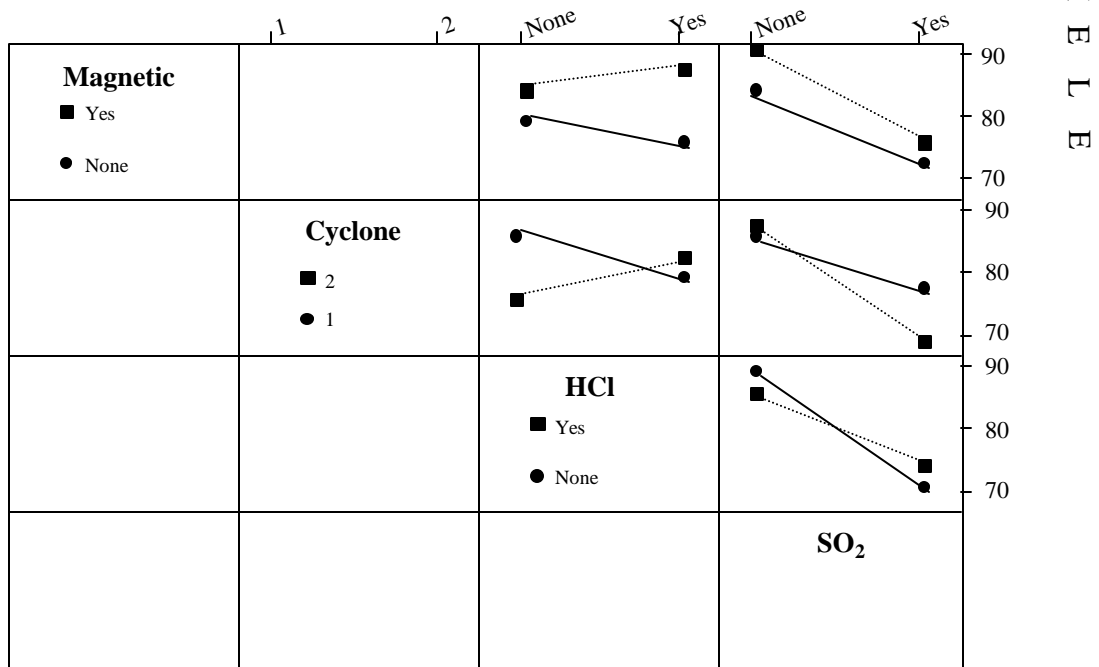

Figure 21. Interaction Plots for Statistical Test Series 5.

The gases noted in Figures 17 and 18 were added to the baseline blend. As can be seen from Figure 17, the nonmagnetic phases in the first cyclone catch were always more catalytic than the magnetic phases in that cyclone catch. However, with the exception of the tests involving the addition of NO_2 and HCl to the baseline blend, the differences observed between the magnetic and nonmagnetic phases were not substantial. When NO_2 and HCl were added to the baseline blend, the amount of oxidized Hg was roughly four times higher when using the nonmagnetic phases versus the magnetic phases.

In Figure 18, the results obtained while using nonmagnetic phases from the first and second cyclone catches of the sized Blacksville fly ash are shown. In three of the four series of tests, more oxidation was observed when using the smaller particle size fraction, although the differences were sometimes minimal. A tendency towards more oxidation with smaller particles would be expected in view of surface area differences between the two size fractions. It is not known why that trend did not hold true when adding NO_2 and HCl to the baseline blend. However, it could potentially be related to the fact that lime (CaO) was higher in the ash from the first cyclone than in any of the other fractions. Since lime can be a good sorbent for HCl, the enrichment of lime in that ash fraction may have affected the results, even though the lime concentration in that ash fraction may not have been very substantial. As noted earlier, the reproducibility was generally excellent for duplicate tests involving the Ontario Hydro method for Hg speciation. It is interesting to note that for both Figures 17 and 18, the data obtained when adding NO_2 and HCl to the baseline blend gave somewhat anomalous results relative to the other plots within a given figure. Thus, special attention should be given to that particular gas mixture in any future tests.

Based on the statistical analyses, the largest impact was clearly from the presence of SO_2 in the simulated flue gas stream (see Figures 19 and 20). The next major factor was whether or not the magnetic or nonmagnetic phases were used. As noted earlier, using the nonmagnetic phases resulted in more Hg oxidation than using the magnetic phases did. This is important because it has been previously suspected that the iron-rich phases are probably more catalytic than the aluminosilicate phases. The only factor that was found *not* to be statistically significant was the *average* effect of HCl (see Figure 19). Although the average effect of HCl was minimal, the presence of HCl was significant in several interactions (see Figure 21) and therefore does play a role in Hg oxidation chemistry. The most dramatic example of the HCl interaction is between HCl and the cyclone fraction.

Results from Combustion Tests

As noted earlier, difficulties with injecting the Blacksville coal precluded combustion tests with that particular coal. Therefore, all combustion testing was performed while firing PRB coal. The PRB coal was successfully fired in the combustor, and no problems were encountered in any aspect of the boiler operation or coal transport into the combustion chamber. Based on data from the on-line gas analyzers, concentrations of various gases in the flue gas stream while burning the PRB coal are given in Table 21 below. No HCl analyses were available for these tests.

Table 21. Concentrations of Selected Gases in PRB Flue Gas.

Gas Species	Concentration (Molar)
CO	30 ppm
CO_2	14%
NO	300 ppm
NO_2	< 5 ppm
O_2	6%
SO_2	100 ppm

During the combustion tests with the PRB coal, the amount of Hg collected in the Ontario Hydro impinger solutions was lower than expected. Although no Hg analyses were performed on the PRB coal used in this study, values of about 50 ppb Hg have been reported for other PRB subbituminous coals. If we assume that 50 ppb Hg is reasonably representative of the PRB coal used in our work, then the amount of Hg collected in the impingers averaged about 40% of the amount expected, assuming that all the Hg was in the gaseous phase. These low recoveries are most likely due to 1) the formation of substantial amounts of particulate Hg, which is then retained in the baghouse, and/or 2) the formation of substantial concentrations of gaseous oxidized Hg which are not effectively transported downstream from the combustor due to wall effects. With respect to the first possibility, other researchers working with PRB coals have reported large percentages (e.g., 40%) of particulate Hg being formed during combustion (19). With respect to the second possibility, it has been speculated that refractory materials in the combustor may catalyze Hg oxidation (16). In small combustors, the ratio of the wall surface area to the combustor volume is relatively high. Therefore, if the refractory materials are indeed catalyzing Hg oxidation, the oxidation effect in small boilers may be quite pronounced. Transport of oxidized Hg species is generally known to be more difficult than transporting elemental Hg, and some researchers have reported indirect evidence that oxidized Hg was being adsorbed onto surfaces within the combustor (16). Studies are needed to identify the magnitude and sources of Hg losses.

Mercury speciation results from the Ontario Hydro testing for the combustion tests (14 tests in all) using PRB coal are shown in Table 22.   For a given set of experimental conditions, tests were performed in duplicate on the same day. In some cases, the tests were repeated (in duplicate) on a different day as well. When more than one day of testing was performed under a given set of conditions, the individual results are grouped according to the day they were performed. Thus, the precision obtained for a given set of conditions on a given day can be seen, as well as the repeatability observed between two different days of testing.

As anticipated, the precision and repeatability for the combustion tests was not as good as for the tests using simulated flue gas streams. For the individual test results, it is interesting to note that the percent oxidized Hg was always higher in the second test performed on a given day under a given set of conditions. This strongly suggests that wall effects were considerable and that those wall effects substantially affected test results. After initially heating up the combustor (to approach thermal equilibrium) for about 48 hours while burning natural gas, coal was always

burned for 1-2 hours before sampling for Hg. Test results suggest that a longer period of time for burning coal prior to testing is needed in order to achieve equilibrium with respect to Hg. It was known that wall effects can complicate issues when working with small boilers for Hg chemistry studies. However, the magnitude of those problems associated with this particular boiler was not known. Potentially, coal may need to be fired for 12 hours or more before Hg equilibration is reached. Based on work performed by the EERC, the heat exchanger may be one source of wall losses, since Hg losses have been observed at such locations. Testing is needed to determine the combustion times necessary to equilibrate the system with respect to Hg speciation. However, monetary and manpower constraints precluded investigations of the necessary equilibration times in this combustor, and also precluded using longer coal combustion periods prior to Hg sampling with the Ontario Hydro sampling train. Nonetheless, a number of observations can be made from the data.

Table 22. Results of Combustion Tests with PRB Coal.

Type of Ash Injected into PRB Flue Gas	Oxidized Hg for Each Test (%)*	Average Oxidized Hg (%)

None
    Day 1
    Day 2
	
	62, 71
	51, 67
		
		63

Whole PRB Fly Ash
    Day 1
    Day 2
	
	26, 27
	9, 14
		
		19

Whole Blacksville Fly Ash	45, 56	50
Nonmagnetic Blacksville Fly Ash	30, 54	42
Magnetic Blacksville Fly Ash	32, 50	41

* Individual data points presented on the same line are for duplicate tests
   performed (in the order shown) on the same day of testing.

One item of interest is that the percent oxidized Hg in the gas stream was fairly high (average of 63%) when firing the PRB coal without any ash injection into the flue gas. Obtaining high levels of oxidized Hg for the PRB flue gas was repeatable on different days of testing. Substantially lower levels of oxidized Hg in the gas phase are typically reported for PRB

coals. One reason for the high levels of oxidized Hg observed in our tests may be related to the chemical composition of the refractory material used in our combustor. As noted previously, other researchers have reported that the refractory material in boilers may catalyze Hg oxidation reactions. This, combined with the high surface area-to-volume ratio of the combustor, may be the primary cause for the levels of oxidized Hg observed. In view of the fact that levels of oxidized Hg were so high in the baseline tests, a variety of plant-specific factors (other than the type of coal being fired) may play a significant role in determining the relative concentrations of different Hg species in the flue gas.

The total Hg collected in the Ontario Hydro impingers was always highest in the tests performed without any ash injections, which probably reflects the sorption capabilities of the fly ashes (i.e., ash may be sorbing some of the vapor phase Hg). When injecting PRB fly ash, the apparent sorption of Hg by the fly ash may not be due entirely to unburned carbon in the ash, since the PRB fly ash used in this study contains less than 0.1% unburned carbon. The Hg capture is probably related to other fly ash components as well, such as the lime in the PRB fly ash. In fact, it is known that some high-calcium fly ashes from western subbituminous coals are good sorbents for Hg (20). When the PRB coal is fired, the inherent fly ash captures a portion of the Hg and is retained in the baghouse. When PRB fly ash is then injected after the first baghouse, additional Hg is presumably captured (from a gas stream already depleted in Hg) and is presumably retained in the second baghouse. Additional work is required to confirm the apparent large percentages of particulate Hg formed during fly ash injection after the first baghouse.

As shown in Table 22, the percentages of oxidized Hg in the flue gas varied considerably as the experimental conditions were changed. The lowest percentage of oxidized Hg (average of 19%) in the flue gas was observed when injecting PRB fly ash into the PRB flue gas stream. This suggests that oxidized Hg was being preferentially captured by the fly ash being injected. The decrease in the percentage of oxidized Hg in the gas stream was not as pronounced when injecting Blacksville fly ash, but was still apparent.

When looking at possible differences in catalytic effects between the PRB and Blacksville fly ashes, tests in which the Blacksville fly ash was injected into the PRB flue gas can not be compared to baseline tests in which no ash was injected into the flue gas. This is because of the attenuation effects associated with apparent Hg sorption by the fly ash during ash injection. Therefore, it is most valid to compare the tests in which PRB fly ash and Blacksville fly ash were injected into the PRB flue gas stream.

Injecting whole Blacksville fly ash into the filtered PRB flue gas appeared to result in greater concentrations of oxidized Hg relative to the tests where whole PRB fly ash was injected. From these data, one might be tempted to conclude that the Blacksville fly ash is more catalytically active than the PRB fly ash. However, those data may be misleading, and definitive conclusions can not be drawn about the relative catalytic effects between the two fly ashes in view of other variables that must be considered. For example, as noted above, the PRB fly ash appears to be a fairly good sorbent for Hg. It is possible that the injected PRB fly ash simply sorbed more oxidized Hg than the injected Blacksville ash did. However, since total Hg recoveries in the impinger solutions were comparable for both sets of tests (injecting PRB fly ash

versus injecting Blacksville fly ash), this explanation is probably not the case. A more likely possibility is the difference in surface areas between the injected PRB and Blacksville fly ashes. As noted earlier, the whole (unfractionated) Blacksville fly ash has considerably more surface area per unit weight than the whole PRB fly ash that was injected. Because the mass injection rate was the same (i.e., about 8 grams/minute) when injecting whole Blacksville and whole PRB fly ashes, more surface area was being injected with the Blacksville fly ash than with the PRB fly ash. Therefore, the increased level of oxidized Hg observed while injecting Blacksville fly ash relative to that observed while injecting PRB fly ash may be primarily related to surface area differences rather than differences in catalytic effects between the two ashes. No testing was performed in an attempt to segregate those variables (i.e., surface area versus relative catalytic activities).

As shown in Table 22, injecting magnetic and nonmagnetic Blacksville fly ash fractions (separated from *whole* fly ash rather than sized fly ash) gave comparable results for the percentages of oxidized Hg in the flue gas stream. Since the magnetic ash has substantially less surface area than the nonmagnetic ash, it could be argued that the magnetic phases must be more catalytic in order to give the same level of Hg oxidation as the nonmagnetic phases. However, it is difficult to draw definitive conclusions about relative catalytic effects between the two ash fractions based on these results. The data scatter (apparently due to wall effects in the combustion system) and the limited number of tests dictate that caution be exercised when viewing these results. Clearly, more work is needed in this area.

Tests with elevated levels of SO_2, NO_x, and HCl (spiked into the flue gas stream) were initially planned. However, performing those tests was not warranted at this time in view of the data scatter observed in the tests performed, combined with uncertainties related to wall losses in the boiler and the low Hg recoveries observed. In addition, work with PRB flue gas by other researchers showed that spiking the flue gas with NO_2 or HCl did not significantly affect Hg speciation (21). Although verification of those results is of interest, it would be unwise to perform those tests until some of the uncertainties (e.g., wall effects) associated with using our combustor for Hg studies are better defined.

CONCLUSIONS

The Hg oxidation chemistry is very complex, both in simulated and actual flue gas streams. The presence of fly ash is a very important factor in Hg oxidation. However, based on results obtained with simulated flue gas streams, large differences in catalytic potential between the two fly ashes studied were generally not observed, even though those fly ash samples were chemically and mineralogically much different from one another. Although the presence of fly ash apparently plays a vital role in Hg oxidation, the flue gas composition may be more important than the ash composition. The critical gas constituents appear to be HCl, NO, NO_2, and SO_2. However, it should not be assumed that those gas species are responsible for the direct oxidation of Hg. Instead, the primary impact of some of those gas species may relate to their potential role in determining concentrations of molecular chlorine and the pool of chlorine atoms, which some researchers believe to be largely responsible for Hg oxidation, particularly in flue gases derived from coals with a significant chlorine content. Catalytic effects from different

fly ashes may be largely attributable to differences in surface areas, and this is an area that should be explored further. Our work to date indicates that the presumed role of iron oxides in the catalytic oxidation of Hg is not as significant as has been postulated by other researchers. Additional work is required to ascertain whether or not the iron-rich phases play a critical role in the Hg oxidation mechanisms, keeping in mind the surface area issues that can complicate data interpretation. When considering the diversity of fly ashes from different sources as well as the diversity in flue gas compositions from coal-fired utility boilers, it is clear that accurately predicting levels of different Hg species in flue gas streams will not be an easy task.

In the combustion tests with PRB coal, apparent wall effects complicated data interpretation. More extensive testing is required to improve statistics and determine sources of Hg "losses" before definitive conclusions can be drawn. This testing should also be broader in scope, and should include sampling prior to the first baghouse as well as sampling between the two baghouses. As with the tests in simulated flue gas streams, issues about surface area complicate data analyses with respect to whether or not the Blacksville fly ash is more catalytic than the PRB fly ash. Any future work should focus more on the amount of surface area being injected per unit time, rather than on the mass injection rates. Also, the formation and collection of particulate Hg is an important consideration with respect to Hg emissions from coal-fired boilers. Work is needed to determine more clearly what the mechanisms are that promote sorption of Hg onto fly ash. This information could be used to develop more effective Hg abatement technologies.

Thus, a number of conclusions can be drawn about Hg speciation chemistry. To reiterate, the following conclusions can be drawn from our work with simulated flue gas and actual coal combustion streams:

- The Hg oxidation chemistry is very complex.

- Large differences in the catalytic potential between the PRB and Blacksville fly ashes were generally not observed.

- Although the presence of fly ash may play a vital role in Hg oxidation, the flue gas composition may be more important than the ash composition.

- HCl, NO, NO_2, and SO_2 are important with respect to Hg speciation chemistry.

- The surface area of the ash may be just as important, or more important, than the ash chemistry or mineralogy.

- The iron-rich ash was not highly catalytic compared to the aluminosilicate-rich phases.

- In the combustion tests, more work is needed to identify sources of Hg losses, to identify the mechanisms involved with those losses (e.g., particulate Hg formation), and to study the importance of ash surface area versus ash chemistry and mineralogy on Hg oxidation.

RECOMMENDED FUTURE WORK

Additional bench-scale work should be performed to study the effects of different *ratios* of various gases on Hg oxidation, as opposed to using *fixed* concentrations of the gases of interest (NO, NO_2, HCl, and SO_2). Catalytic effects from different fly ashes may be largely attributable to differences in surface areas, and this is an area that should be explored further. Additional work is required to ascertain whether or not the iron-rich phases play a critical role in the Hg oxidation mechanisms, keeping in mind the surface area issues that can complicate data interpretation. For the combustor used in this study, more extensive testing should be performed to determine sources of Hg "losses", help identify mechanisms for those losses, and determine the importance of ash surface area versus ash chemistry and mineralogy on Hg oxidation mechanisms. With respect to the later point, future work should focus more on the amount of surface area being injected per unit time, rather than on the mass injection rates of fly ash. Work is needed to determine more clearly what the mechanisms are that promote sorption of Hg onto fly ash. Finally, more work is needed in the development of gas conditioning units for Hg CEMs in order to provide reliable and low-maintenance systems suitable for use by the electric utility industry.

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APPENDIX 1

Typical Results (Dry Basis) for Proximate/Ultimate Analyses on the PRB Coal

Ash	6.2 %
Volatile Matter	43 %
Fixed Carbon	51%
Total Carbon	69 %
Hydrogen	4.7 %
Nitrogen	0.9 %
Chlorine	0.03 %
Oxygen	19 %
Sulfur	0.30 %
Heating Value	12,100 Btu/lb

APPENDIX 2

X-ray Diffraction Results for the Blacksville and PRB Fly Ash Samples*

Fly Ash Sample	Minerals Detected
Blacksville, Whole Ash	Quartz (SiO_2), Mullite ($Al_6Si_2O_{13}$), Magnetite (Fe_3O_4), Hematite (Fe_2O_3) Trace of Lime (CaO), Trace of Anhydrite? ($CaSO_4$)
Blacksville, Cyclone 1, Magnetic	Magnetite (Fe_3O_4), Hematite (Fe_2O_3) Quartz (SiO_2), Mullite ($Al_6Si_2O_{13}$)
Blacksville, Cyclone 1, Nonmagnetic	Quartz (SiO_2), Mullite ($Al_6Si_2O_{13}$) Magnetite (Fe_3O_4), Hematite (Fe_2O_3) Lime (CaO) Trace of Anhydrite? ($CaSO_4$)
Blacksville, Cyclone 2 (all nonmag.)	Quartz (SiO_2), Mullite ($Al_6Si_2O_{13}$) Magnetite (Fe_3O_4), Hematite (Fe_2O_3) Trace of Anhydrite? ($CaSO_4$)
PRB, Whole Ash (all nonmagnetic)	Quartz (SiO_2) Lime (CaO), Periclase (MgO), Calcium Aluminum Oxide ($Ca_3Al_2O_6$) Trace of Anhydrite? ($CaSO_4$)
PRB, Cyclone 1 (all nonmagnetic)	Quartz (SiO_2) Lime (CaO), Periclase (MgO), Calcium Aluminum Oxide ($Ca_3Al_2O_6$) Trace of Anhydrite? ($CaSO_4$)
PRB, Cyclone 2 (all nonmagnetic)	Lime (CaO), Periclase (MgO), Calcium Aluminum Oxide ($Ca_3Al_2O_6$), Anhydrite ($CaSO_4$) Quartz (SiO_2)

* For each ash sample, the minerals are roughly grouped to show approximate relative concentrations. For example, the Blacksville ash from Cyclone 2 had relatively large amounts of quartz and mullite, lesser amounts of magnetite and hematite, and possibly a trace of anhydrite.